

# CHEMISTRY

## *A Textbook for Class XI*

### Part II

#### Authors

K. N. Ganesh	Puran Chand
V Krishnan	K. V Sane
S S Krishnamurthy	R. D Shukla
M Nagarajan	V N P. Srivastava
B. Prakash	B Venkataraman

#### Editors

C N R Rao      K V. Sane

R D Shukla



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## Chemistry Writing Group

Prof C. N. R. Rao, F.R.S. (*Chairman*)

Director

Indian Institute of Science

Bangalore

Dr K. N. Ganesh

National Chemical Laboratory

Pune

Prof. V. Krishnan

Indian Institute of Science

Bangalore

Prof. R. D. Shukla (*Coordinator*)

National Council of Educational

Research and Training

New Delhi

Prof. K. V. Sane

Delhi University

Delhi

Dr V. N. P. Srivastava

National Council of Educational

Research and Training

New Delhi

Prof S. S. Krishnamurthy

Indian Institute of Science

Bangalore

Dr. Puran Chand

National Council of Educational

Research and Training

New Delhi

Prof. B. Venkataraman

Tata Institute of Fundamental

Research

Bombay

Dr B. Prakash

National Council of Educational

Research and Training

New Delhi

Dr M. Nagarajan

University of Hyderabad

Hyderabad



## Foreword

The National Policy on Education (NPE) 1986 has emphasized the need for qualitative improvement of school education particularly in the area of Science and Mathematics Education. The Government of India has already initiated a number of steps in this direction. The National Council of Educational Research and Training (NCERT) has been assigned the responsibility of developing a new curriculum and related curricular materials in line with the new education policy to serve as a model for the States and the Union Territories to adopt/adapt.

The Council set up an Advisory Committee under the chairmanship of Prof. C. N. R. Rao, Director, Indian Institute of Science, Bangalore, and Chairman of the Prime Minister's Scientific Advisory Committee, for developing instructional package in science and mathematics from upper primary to senior secondary stage. On the advice of the Committee, different writing teams headed by eminent scientists were formed. At senior secondary level Prof. Rao accepted the invitation of NCERT to work as the chairman of Chemistry Writing Team and to take the responsibility of developing curriculum package in Chemistry. The Chemistry Writing Team consisted of distinguished Chemistry experts from universities, research institutes and NCERT.

The writing team, while developing the present syllabus and the textbook, considered the feedback regarding syllabus and textbooks in vogue. After the textbook was developed, it was exposed to a teachers' workshop to have their comments and suggestions. Suggestions of the teachers were incorporated, wherever possible, before the final manuscript was sent for publication.

I am indeed very thankful to Prof. C. N. R. Rao, who took the leadership of Chemistry team and provided valuable guidance to his team of authors and finally edited the manuscript with Prof. K. V. Sane and Prof. R. D. Shukla. I am grateful to Prof. V. Krishnan, Prof. B. Venkataraman, Prof. K. V. Sane, Prof. S. S. Krishnamurthy, Dr. M. Nagarajan, Dr. K. N. Ganesh, Prof. R. D. Shukla, Dr. V. N. P. Srivastava, Dr. Puran Chand, and Dr. B. Prakash who authored different parts of the book. My colleagues in the Department of Education in Science and Mathematics, Prof. R. D. Shukla (Coordinator), Dr. V. N. P. Srivastava, Dr. Puran Chand and Dr. B. Prakash took a lot of pains in shaping the manuscript in the pressworthy form and saw it through the press. I am grateful to all of them.

I am very much indebted to the teachers (acknowledged elsewhere) who participated in review workshop and provided valuable suggestions and comments for the improvement of the draft manuscript. I must make a special mention of Prof. A K Jalaluddin, Joint Director, NCERT, and Prof. B Ganguly, Head, Department of Education in Science and Mathematics, who took a lot of interest in this project and extended all possible help in bringing out this book. I also express my thanks to Shri C. N Rao, Head, Publication Department, and his publication team for making all efforts in bringing out this book in a good form.

Curriculum development is a highly challenging task. No one can claim to have developed a perfect curriculum or curricular materials. Although Prof. C N. R Rao and his competent team members did a very good job of writing this book in line with NPE, there can always be some scope for further improvement. I, therefore, request all those who will be using this book to evaluate the materials with an open mind and offer their valuable suggestions, for further improvement.

P.L. MALHOTRA

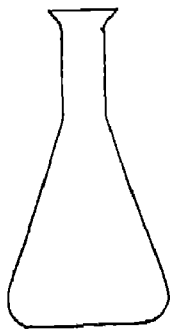
*Director*

National Council of Educational  
Research and Training

New Delhi  
12 July 1988

## Preface

In this introductory book, we have expounded the principles of modern chemistry in the simplest possible language and also illustrated how chemical systems behave and react. More importantly, we have indicated, wherever possible,



SOLUTIONS  
TO  
PROBLEMS  
CHEMISTRY

how chemistry works for man. In presenting chemistry in this manner, we have adopted several strategies. We have given analogies and solved examples; we have also shown how principles come about by describing simple experiments. The strategy has varied with subject matter. We hope to review this book after receiving the reaction from students and teachers to this trial edition. In the meantime, we hope the book will be found useful by students and teachers whose response is of great value to us.

Chemistry deals with the preparation, properties, structure and reactions of material substances. Since diverse substances are present in Nature and in every day life, the scope of chemistry is immense. Chemistry has interfaces with all scientific disciplines and a knowledge of the subject is essential for understanding Nature as well as for the progress of society. A well-trained chemist can not only contribute to the growth of chemical science and industry, but also to other emerging areas of science such as biotechnology and materials science. The future of our society will depend on the availability of such chemists. There is no better way to describe the indispensable role of chemistry than to quote from a lecture delivered by Nobel Laureate George Porter some time ago

Throughout history, the lot of most of mankind has been rather miserable. Until a few centuries ago it was really slavery and into the last century, although legally free, most men and women had to labour so hard to earn a living that they were effectively slaves to their work. Different professions have had different approaches to this problem. As (Nobel Laureate) Max Perutz has put it "The priest persuades the humble people to endure their hard lot, the politician urges them to rebel against it and the scientist thinks of a method that does away with the hard lot altogether"

No branch of science has done more, or promises more, in this respect, than chemistry. It has provided a cornucopia of good things, both of necessities and

luxuries, which have improved our health, and our wealth and also, I believe, our happiness. Man is himself a biochemical system living in a chemical world. His health has been improved out of all recognition by better nutrition, better hygiene and by the drugs which have doubled his lifespan, relieved pain and made it possible for many handicapped people to lead a more normal life.

His wealth, judged in terms of the general availability of the necessities of life, is many times what it was even a few decades ago. This is particularly true of the wealth of food now available in countries which, only a few years ago, were poor to the point of starvation.

Most people today would also class as necessities the plastics, fibres and paints which have made it possible for everybody to be well clothed (though not all may want it!) and to live in a bright, clean environment without having to employ the labour of others to keep it so.

The luxuries, which are also fast becoming universal, often owe as much to chemistry as to the other technologies. This is obvious of such things as motor fuels, cosmetics and dyestuffs but it is also true of electronic devices of every kind, and mechanical, labour-saving appliances. Some of the largest manufacturers of heavy electrical equipment employ more chemists than physicists and, on the newer and lighter side, the silicon *chip* is a highly purified chemical element treated with other elements in a very sophisticated, chemically pure environment.

But perhaps the most successful of all, over the last two or three decades, has been the contribution of chemistry to agriculture. The Green Revolution did exactly what the king of Brobdingnag of *Gulliver's Travels* had asked for and "made two ears of corn or two blades of grass grow where only one grew before" and those who brought it about, according to the king, "would deserve better of mankind and do a more essential service for the country than a whole race of politicians put together". This was a proud achievement of chemistry, depending heavily on fertilizers and new insecticides, plant growth substances and the like. It is a huge industry. The world production of plant food has increased threefold in the last 20 years. India is effectively self-sufficient in food.

We hope that we have succeeded, at least partly, in presenting the flavour of modern chemistry in this book. We look forward to the suggestion of students and teachers for improving the text.

C.N.R. RAO  
Chairman  
Chemistry Writing Group



**National Workshop for Review of Class XI  
Chemistry Textbook (30 October-3 November 1987)**

**LIST OF PARTICIPANTS**

- |   |   |
|---|---|
| 1 Prof C N. R. Rao<br>Director<br>Indian Institute of Science<br>Bangalore                          | 7. Dr V S Parmar<br>Reader in Chemistry<br>University of Delhi<br>Delhi-110007  |
| 2. Smt U Mutreja<br>PGT (Chemistry)<br>Sardar Patel Vidyalaya<br>Lodi Estate<br>New Delhi-110003    | 8 Shri C L Verma<br>Lecturer in Chemistry<br>Govt. Sr Sec School<br>Banikhet<br>P O Banikhet<br>Distt. Chamba (H. P.) |
| 3 Dr. K N Upadhyaya<br>Chemistry Department<br>Ramjas College<br>(Delhi University)<br>Delhi-110007 | 9 Dr (Smt ) Nayantara Chhetroy<br>Lecturer in Chemistry<br>Regional College of Education<br>Bhubaneswar               |
| 4 Shri P K Sharma<br>PGT Chemistry<br>Kendriya Vidyalaya<br>Lawrence Road<br>Delhi                  | 10. Dr Rajan Bandiwar<br>Master in Chemistry<br>Sainik School<br>Rewa-486001 (M. P )                                  |
| 5. Shri P P Singh<br>Principal<br>Bareilly College<br>Bareilly (U. P )                              | 11 Dr J D Pandey<br>Reader<br>Department of Chemistry<br>Allahabad University<br>Allahabad                            |
| 6 Smt Usha Kiran Jetly<br>PGT (Chemistry)<br>Kendriya Vidyalaya<br>New Mehrauli Road<br>New Delhi   | 12 Shri D C Grover<br>Lecturer in Chemistry<br>SCERT, Sohna Road<br>Gurgaon (Haryana)                                 |

- 13 Dr A. K. Kaushal  
PGT Chemistry  
Army Public School  
New Delhi-110010
14. Shri R. D Saxena  
Jr. Science Counsellor  
Department of Science Education  
SCERT  
3, Link Road, Karol Bagh  
New Delhi-110005
- 15 Prof S N Mishra  
Professor and Head  
University of Bhavnagar  
Bhavnagar (Gujarat)
- 16 Prof H G. Krishnamurthy  
Department of Chemistry  
University of Delhi  
Delhi-7
- 17 Shri Shiv Kumar  
Sr Chemistry teacher  
Delhi Public School  
Mathura Road, New Delhi
- 18 Prof K. N. Mehrotra  
Department of Chemistry  
Agra University, Agra
- 19 Shri Bhim Sain  
Lecturer in Chemistry  
Govt. College  
Jind (Haryana)
- 20 Dr B Sharma  
Reader  
Chemistry Department  
University of Gorakhpur  
Gorakhpur-273009
21. Shri M K Kulshreshtha  
PGT Chemistry  
Kendriya Vidyalaya  
Mathura Cantt., Mathura (U P)
- 22 Prof M L Dhar  
Department of Chemistry  
University of Jammu  
Jammu
23. Prof. K. C. Joshi  
Emeritus Scientist  
Chemistry Department  
University of Rajasthan  
Jaipur-302004
24. Shri S. K. Singhal  
PGT (Chemistry)  
G. M. Govt Sr. Sec. School  
Shahdra  
Delhi-32
25. Ms. Shubha Kesavan  
PGT Chemistry  
Demonstration School  
Regional College of Education  
Mysore-7
26. Shri R. K. Bali  
PGT Chemistry  
Nav Hind Girls Sr. Sec. School  
New Rohtak Road  
New Delhi-110005
27. Prof. B. Venkataraman  
Sr. Professor  
Tata Institute of Fundamental  
Research  
Bombay-400005
- 28 Shri M. Nagrajan  
Reader in Chemistry  
School of Chemistry  
University of Hyderabad  
Hyderabad-500 134
29. Shri K. N. Ganesh  
Scientist E-II  
Organic Chemistry Div. I  
National Chemical Laboratory  
Pune-411008

- 30 Prof S S Krishnamurthy  
Professor in Chemistry  
Deptt of Inorganic and  
Physical Chemistry  
Indian Institute of Science  
Bangalore-560012
- 31 Prof V Krishnan  
Professor in Chemistry  
Department of Inorganic and  
Physical Chemistry  
Indian Institute of Science  
Bangalore-560012
- 32 Prof P K Sen  
Professor and Head  
Chemistry Department  
Presidency College  
Calcutta-73
- 33 Shri K V. Sane  
Professor in Chemistry  
Delhi University  
Delhi-110007
34. Prof D. D. Mishra  
Head  
Department of Chemistry  
R D University  
Jabalpur  
Jabalpur (M. P )
- 35 Dr Raj Kishore Shukla  
Sr Lecturer  
Department of Chemistry  
Atarra Post Graduate College  
Atarra-210201, Banda, U P
- 36 Shri Ramesh Sharma  
Lecturer (Chemistry)  
State Institute of Science  
Education Punjab  
Chandigarh
- 37 Dr R K Dewan  
Professor  
Chemistry Department  
Panjab University  
Chandigarh
38. Prof. B. D. Atreya  
MMTC Colony  
New Delhi

*NCERT Faculty*

1. Prof R D. Shukla (Coordinator)
2. Dr V. N P. Srivastava
3. Dr Brahm Parkash
- 4 Dr Puran Chand



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## UNIT 11

# RATES OF CHEMICAL REACTIONS

*Since it is Nature's law to change,  
Constancy alone is strange.*

### OBJECTIVES

In this Unit, we shall learn

- \* to express the rate of a chemical reaction;
- \* the various factors affecting the rate of a chemical reaction;
- \* the meaning of energy of activation of a chemical reaction;
- \* the effect of a catalyst on the rate of a reaction.

WHETHER A REACTION will proceed in a particular direction and to what extent is decided by the tendency to decrease energy and to increase disorder. We saw earlier that there should be a decrease in free energy ( $\Delta G < 0$ ) for the reaction to be spontaneous. Even though there may be a decrease in free energy, reactants do not always proceed to form products instantaneously and it is observed that different reactions take place at different rates. The rate of formation of products or the rate of disappearance of reactants depends mainly on the rate at which molecules of the reactants encounter each other, and on the temperature of the system. In this Unit, we shall attempt to understand the reasons for this dependence, and how experimental variables, such as concentration of reactants, particle size, temperature, the presence or absence of a catalyst determine the rate of a reaction.

### 11.1 RATE OF A REACTION

The rate of disappearance of reactants can be experimentally measured, so can we determine the rate of appearance of products. The rate of a chemical reaction can be expressed as *The amount of reactant used up in a given time or the amount of product formed in a given time.* For example, in the reaction between acetic acid and methanol in aqueous solution to form methyl acetate



we can measure the rate of the reaction by determining the rate at which acetic acid disappears or the rate at which methanol disappears or the rate at which methyl acetate forms. A convenient unit to express the rate is moles per second ( $\text{mol sec}^{-1}$ ) or to state in terms of concentration,  $\text{mol litre}^{-1}\text{sec}^{-1}$ .

#### Example 11.1

In a typical experiment carried out at 298 K, 500  $\text{cm}^3$  of 1M solution of acetic acid was mixed with 500  $\text{cm}^3$  of 1M solution of methanol and the concentration of acetic acid and methyl acetate were determined as a function of time. The observations are given below:

Temperature = 298K

Time (seconds)	Concentration of acetic acid ( $\text{mol L}^{-1}$ )	Concentration of methyl acetate ( $\text{mol L}^{-1}$ )
0 (Time of mixing)	0.500	0
2	0.442	0.054
4	0.405	0.101
6	0.372	0.135
8	0.338	0.165
10	0.321	0.182
12	0.290	0.211
14	0.275	0.225
16	0.258	0.242

Time (seconds)	Concentration of acetic acid (mol L <sup>-1</sup> )	Concentration of methyl acetate (mol L <sup>-1</sup> )
18	0.241	0.261
20	0.228	0.271
25	0.201	0.292
30	0.181	0.322
35	0.163	0.336
40	0.148	0.352
45	0.137	0.366
50	0.125	0.375
60	0.110	0.392
70	0.098	0.404
80	0.088	0.413
90	0.080	0.425
100	0.073	0.428
110	0.065	0.430
120	0.058	0.440

We plot the concentration of acetic acid and methyl acetate as a function of time and obtain Fig. 11.1.

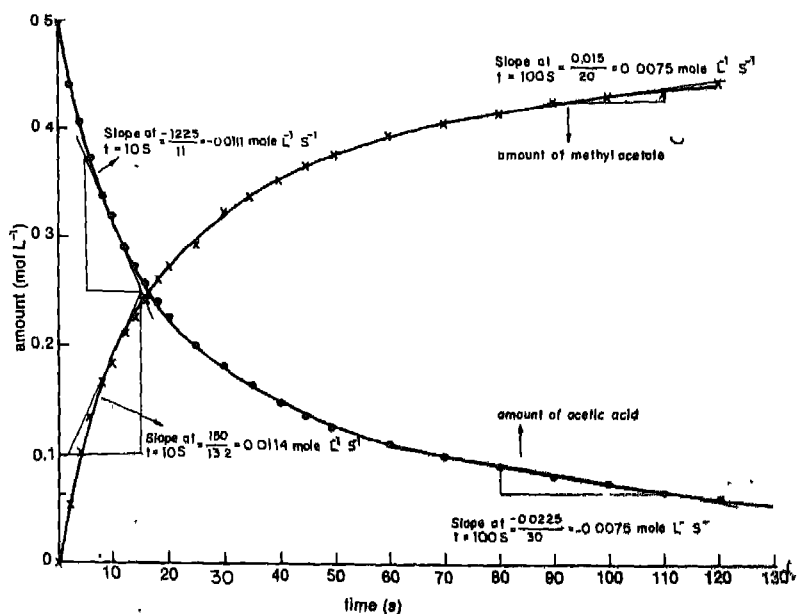


Fig. 11.1 Plot of concentrations of acetic acid and methyl acetate as a function of time

The rate of the reaction is the rate of disappearance of the reactant (acetic acid) or the rate of formation of the product (methyl acetate). The instantaneous rate at any time is given by the slopes of either of the two curves at the points corresponding to the time and this is done by drawing the tangent to the two curves and calculating the slopes of the tangents. The following points should be verified

- (1) The amount of acetic acid reacted = the amount of methyl acetate formed at any given time
- (2) The rate of disappearance of acetic acid = the rate of formation of methyl acetate = the rate of reaction
- (3) The rate of reaction is not constant but decreases with time. It is also possible to calculate an average rate at a given time from the data given by taking the difference in concentrations at two equidistant points in time and calculating an average rate of change. For example, to calculate an average rate at 10 seconds, we take the reading at 8 and 12 seconds and divide by 4. The rate of

disappearance of acetic acid =  $\frac{0.338 - 0.290}{4} = 0.012 \text{ mol L}^{-1} \text{ s}^{-1}$  The rate of

appearance of methyl acetate =  $\frac{0.211 - 0.165}{4} = 0.012 \text{ mol L}^{-1} \text{ s}^{-1}$

The following table is to be constructed from the data fill in the blanks:

Time (in seconds)	Amount of acetic acid reacted (mol L <sup>-1</sup> )	Amount of methyl acetate formed (mol L <sup>-1</sup> )	Instantaneous rate of reaction (mol L <sup>-1</sup> )		Average rate of reaction (mol L <sup>-1</sup> )	
			Rate of disappear- ance of acetic acid	Rate of forma- tion of methyl acetate	Rate of disap- pearance of acetic acid	Rate of formation of methyl acetate
10	0.179	0.182	0.0111	0.0114	0.012	0.012
20	0.272	0.271	---	---	---	---
40	0.319	0.322	---	---	0.0026	0.0026
60	0.390	0.392	---	---	---	---
80	0.412	0.413	---	---	0.009	0.0010
100	0.427	0.428	0.0075	0.0075	0.00075	0.00025
120	0.442	0.440	---	---	---	---

Another method to estimate an average rate of the reaction, is to find out the time taken for a certain per cent (say 10%) of the reactant to disappear and construct the following table and then calculate the average rate of reaction as the concentration changes

$\% \text{ reacted}$	Amount of acetic acid reacted ( $\text{mol l}^{-1}$ )	Time taken (s)	Average rate of reaction ( $\text{mol l}^{-1} \text{ s}^{-1}$ )
0-10	0.05	1.7	0.029
10-20	0.10	2.5	0.020
20-30	0.15	3.0	0.017
30-40	0.20	4.2	0.012
40-50	0.25	4.8	0.010
50-60	0.30	8.8	0.0057
60-70	0.35	15.0	0.0031
70-80	0.40	27.5	0.0018
80-90	0.45	68.0	0.00073

Most reactions slow down as they proceed (When do exceptions occur?—when the product can catalyse the reaction) This is a direct consequence of the fact that reactions can occur only on the encounter of reactant molecules and the rate of encounter will decrease with decrease in the concentration of the reactants. Since the reaction rate is not constant, it is meaningless to talk about the rate of reaction between methanol and acetic acid unless we specify concentration and temperature. To compare rates of different reactions we could compare the rates at a specified concentration of reactants (say  $1 \text{ mol l}^{-1}$  for all the reactants) or compare the times it takes for the reactions to go to completion when we start with the same concentration of reactants. The second method is difficult since most reactions slow down as they proceed. One, therefore, compares the times it takes for the reactions to proceed to a definite stage, say 98 per cent completion. This time is denoted as the reaction LIFE TIME. The shorter the reaction life time, the faster the reaction. A modification of this method is to compare the time it takes for the reaction to proceed midway (50% completion).

In our example above, determine the time for the reaction to proceed midway and the reaction life time (98% completion).

## 11.2 INSTANTANEOUS RATE OF A REACTION AND ORDER OF A REACTION

In the previous section we noted that the rate of reaction decreases with time since the concentration of the reactants keeps decreasing with time. We determine the instantaneous rate by measuring the slopes of the tangents to the curves (Fig 11.1) at that instant of time.

For a particular reaction



we can express the rate of reaction as the rate of decrease of A or of B or as the rate of increase of C or D.

The different rates are identical if the stoichiometric coefficients of the different species participating in the reaction are the same. (For example, the stoichiometric

coefficients of all the species A, B, C, D are unity in the above reaction ) However, if  
 $A + B \rightarrow 2C$ ,

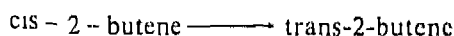
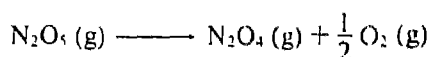
then the rate of disappearance of A = rate of disappearance of B =  $1/2$  (rate of appearance of C) In most cases, these rates are some functions of concentration of the reactants. In simple cases, they can be written as, rate of reaction =  $k c_A^x c_B^y$ , where  $c_A$  and  $c_B$  are concentrations of reactants and  $x$  and  $y$  represent the powers to which the concentrations are raised.  $k$  is a constant called the RATE CONSTANT. We call  $x$  and  $y$  as the order of the reaction with respect to reactant A and B respectively. For example, it may be found that

$$\text{Rate} = k (c_A)^1 (c_B)^2$$

Then we say that the reaction is first order with respect to reactant A and second order with respect to reactant B and the overall order is 3

### 11.3 FACTORS AFFECTING THE RATE OF A REACTION

We have stated that the rate of reaction between two reactants depends on the rate of encounter between the molecules of the reactants. If three reactants are involved in a reaction, simultaneous encounter of three molecules is a very rare process and very often the overall reaction in such cases is the result of two or more simpler processes, each involving not more than two molecules. We shall not consider such complex cases. Nor shall we discuss those cases where only one reactant is involved such as in the decomposition or the isomerisation of a reactant:



Even in such systems, molecular collisions are involved, but we shall avoid consideration of such cases in this book. Those experimental conditions of encounter between reactant molecules would thus aff.

#### 11.3.1 Factors Affecting Rate of Encounters between Reactant Molecules

##### (1) Concentration of reactants

In three test tubes we take the following

5 cm<sup>3</sup> of 1 M hydrochloric acid solution

2.5 cm<sup>3</sup> of 2 M hydrochloric acid solution

10 cm<sup>3</sup> of 0.5 M hydrochloric acid solution.

A magnesium wire (3 cm length) is cleaned and cut into three pieces of equal length (about 1 cm). Let us compare the rate of evolution of gas bubbles. Although we have started with the same number of moles of hydrochloric acid in each case and we have also added almost equal amounts of magnesium to each test tube, we find that the rate of evolution of gas is faster with the more concentrated solution of the acid (2.5 cm<sup>3</sup> of 2M HCl). Is it possible to explain this effect in terms of the rate of encounter between the reacting molecules?

We reach the conclusion that an increase in concentration of reactants increases the rate of the reaction

In reactions in the gas-phase, increase in pressure of the reactant gases should increase the rate for the same reaction. The number of molecules per unit volume increases with increase in pressure and the rate of encounter between reactant molecules would hence increase.

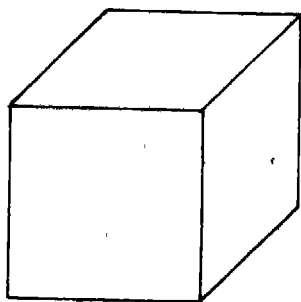
(2) *Increasing the possibility of molecules of reactants coming near each other*

In two watch glasses (about 8 cm diameter) let us make a *heap* of one gram of potassium permanganate. In the first watch glass, we shall choose as large crystals as possible to make up the weight. The potassium permanganate in the second watch glass is finely powdered using a pestle and mortar before making up the heap. To each watch glass we add two drops of glycerol on the top of the heap. We shall observe that in the latter case the reaction proceeds violently (caution, heat and fire are involved).

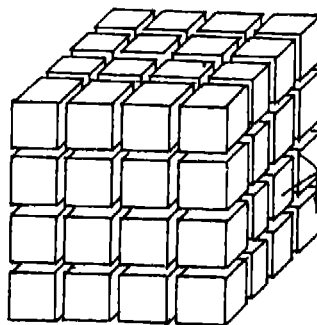
Let us compare the times taken to dissolve 1 g of crystals of sugar (rock candy—*kadisakkar*) and 1 g of powdered sugar in 100 cm<sup>3</sup> of water.

In both cases it is observed that the rate of the process is increased when the particle size of the solid state is decreased. This is easily explained when we consider the surface area of the solid in contact with the liquid under the two conditions. To illustrate this point, consider the following three cases:

1. For a cube of dimension (4 cm × 4 cm × 4 cm)  
The total surface area =  $4 \times 4 \times 6 \text{ faces} = 96 \text{ cm}^2$   
Total volume =  $64 \text{ cm}^3$
2. For 64 cubes of dimension (1 cm × 1 cm × 1 cm)  
The total surface area =  $64 \times 6 \text{ cm}^2 = 384 \text{ cm}^2$   
Total volume =  $64 \times 1 \text{ cm}^3 = 64 \text{ cm}^3$
3. For 64000 cubes of dimension (0.1 cm × 0.1 cm × 0.1 cm)  
The total surface area =  $64000 \times 6 \times 10^{-2} \text{ cm}^2 = 3840 \text{ cm}^2$   
Total volume =  $64000 \times 10^{-3} \text{ cm}^3 = 64 \text{ cm}^3$



(a) surface area =  $6 \times 4 \times 4 = 96 \text{ cm}^2$   
volume =  $4 \times 4 \times 4 = 64 \text{ cm}^3$



(b) surface area =  $64 \times 6 \times 1 \times 1 \text{ cm}^2 = 384 \text{ cm}^2$   
volume =  $64 \times 1 \times 1 \times 1 \text{ cm}^3 = 64 \text{ cm}^3$

**Fig. 11.2** The diagram depicts how decreasing the particle size of a solid (keeping the total volume constant) results in an increase in area

This calculation demonstrates that decreasing the particle size of a solid (keeping the total volume, and hence the mass, constant) increases the area of contact between the solid particles and their surroundings. Systems where the reactants are not uniformly dispersed in each other are known as HETEROGENEOUS SYSTEMS. In heterogeneous systems the rate of reaction will depend upon the area of contact between the reactants. In a solid-gas or solid-liquid system, the fineness of the solid particles determines the rate of the reaction—the finer the particle the faster the rate. This principle is used in the manufacture of explosives and rocket fuels. One of the common industrial accidents is the explosion that occurs when an inflammable substance is finely dispersed in a room.

A corollary to our discussion is that two reactants will react faster when the reaction is ... this leads to the maximum ... . Increasing the fineness of the solid sample is an attempt to decrease the heterogeneity of the reaction mixture. A reaction will proceed faster if the reactants are mixed in the liquid phase (or solution phase) than when carried out under heterogeneous conditions, provided the concentrations are the same. Let us perform the following experiments to illustrate this principle:

- On a layer of 0.5 g of lead nitrate crystals spread a layer of 0.5 g of potassium iodide crystals
- Grind separately 0.5 g of lead nitrate and 0.5 g of potassium iodide to a fine powder and mix them well with a spatula or spoon
- Dissolve 0.5 g of lead nitrate and 0.5 g of potassium iodide separately in 5 cm<sup>3</sup> of water (in each case) and mix the two solutions.

The rates of formation of lead iodide in the three cases would be found to increase from (a) to (c).

It is common knowledge that one stirs tea to dissolve the sugar quickly. The same is true when we mix two reactants.

To sum up, the rate of a reaction is decided by the rate of encounter between the reactant molecules: (a) in case of solid-liquid or solid-gas heterogeneous systems decreasing the particle size of the solid and thus increasing the area of contact between reactants increases the rate; (b) increasing the concentration of reactants in solution or increasing the pressure of gases increases the rate; (c) stirring or mixing two reactants also increases the rate because of increased dispersion of one reactant species in the other.

### 11.3.2 Effect of Temperature on the Reaction Rate

One obvious way to increase the energy of the reactant molecules is to increase the temperature at which the reaction is carried out. We know that the kinetic energy of the molecules increases with increase in temperature. Increase in temperature also leads to increase in the rate of collisions between molecules and the rate of diffusion of molecules, and should therefore automatically lead to an increase in reaction rate. However, a simple calculation shows that the magnitude of the increase in the rate of a reaction is very much more than what we would predict from the kinetic theory



which tells us about the rates of collisions and rates of diffusion.

Let us assume that we changed the temperature of a reaction from 27° to 37° C, i.e. from 300 K to 310 K. Kinetic theory predicts that the average kinetic energy is proportional to the absolute temperature. Hence the increase in kinetic energy  $= \frac{10\text{K}}{300\text{K}} \times 100 = 3.3\%$ . Since the kinetic energy of a molecule is  $\frac{1}{2}mv^2$ , where  $m$  is the mass of the molecule and  $v$  its velocity, the velocity of the molecules is increased by  $\sqrt{3.3\%}$  i.e., 1.8%. Since the rate of encounter between molecules is directly proportional to their speeds, we should expect that the rate of reaction is increased by 1.8% when we change the temperature by 10K near 300 K. This predicted change is much smaller than the two-to five-fold increase in reaction rates observed in most reactions for an increase of 10K in temperature near 300 K. We therefore conclude that increase in the rate of encounters is not the only thing that affects the rate of reaction when the temperature of the reaction is increased.

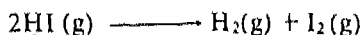
A very simple experiment can be performed to demonstrate the effect of temperature on the rate of reaction. Let us take three 100 cm<sup>3</sup> beakers containing 30 cm<sup>3</sup> of 0.5 M oxalic acid solution to which 5 cm<sup>3</sup> of dilute sulphuric acid has been added. One of the beakers is kept in a bath of ice and water and the other at room temperature. The third one is warmed to about 70°C. A few drops of 0.1 M potassium permanganate solution are added to each one of the three beakers. The times taken for the permanganate to decolorise would be very different in the three cases.

A systematic study of the dependence of the rates of reactions on temperature as in the above example led the Swedish scientist, Svante Arrhenius, to propose the following.

- Every encounter between reactant molecules does not lead to a reaction resulting in a product.
- The energy of the colliding molecules should be greater than what he called the ACTIVATION ENERGY, for an encounter to be effective in producing a product.

Thus this theory, known as the Arrhenius theory of reaction-rate, predicts that the reaction rate should increase with increase in energy of the reactant molecules.

Bodenstein (1899) carried out measurements of rates of the decomposition reaction of hydrogen iodide:



The following rates are calculated from his experimental data and the kinetic theory of gases:

Temperature (K)	Rate of collisions between molecules (per cm <sup>3</sup> per second)	Rate of reaction (molecules reacting per cm <sup>3</sup> per second)	Fraction of encounters between reactants leading to products
573	$6.10 \times 10^{31}$	$1.75 \times 10^{15}$	$2.9 \times 10^{-17}$
673	$6.61 \times 10^{31}$	$5.03 \times 10^{17}$	$7.6 \times 10^{-15}$
773	$7.08 \times 10^{31}$	$4.59 \times 10^{19}$	$6.5 \times 10^{-11}$

It is significant to note that the fraction of successful encounters increases by a factor of hundred when the temperature is increased by  $100^{\circ}\text{C}$ ; however, the rate of encounters increases by only about 7%.

*Arrhenius theory of reaction rates.* The distribution of energy among the colliding particles can be calculated and is shown in Fig. 11.3

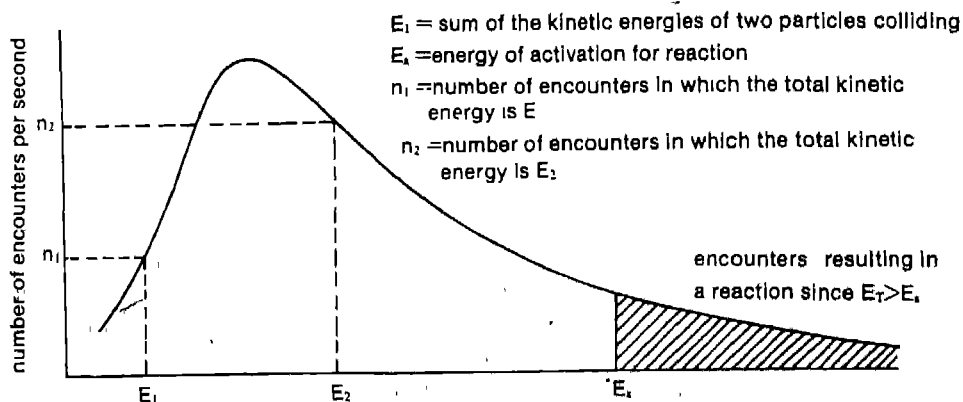


Fig. 11.3 Distribution of energy among colliding particles

What Arrhenius postulated was that the reactants would not transform to products unless the energy of the colliding particles were greater than a certain value called the ENERGY OF ACTIVATION. A plot at different temperature shows how the fraction of colliding molecules that have energies greater than the energy of activation, and hence can transform to products, increases with temperature.

The effect on the reaction rate of this increase in the fraction of molecules exceeding the threshold energy with temperature, is much larger than the marginal

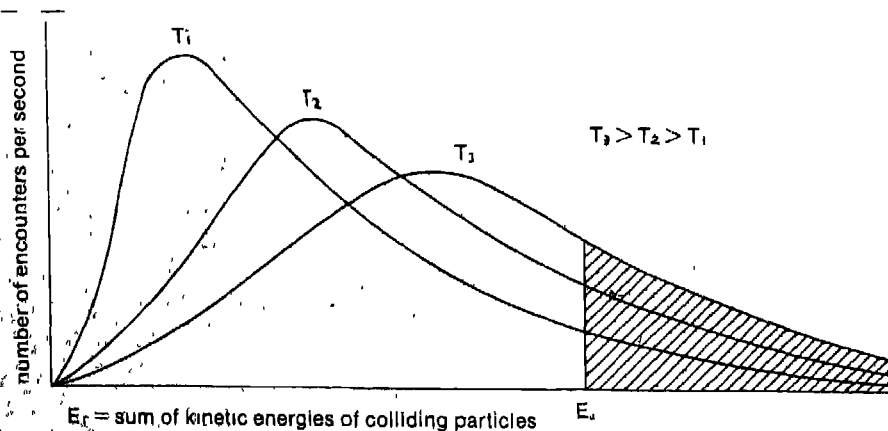
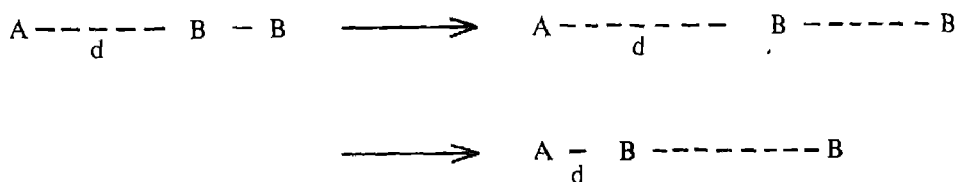


Fig. 11.4 Distribution of collision energies at three different temperatures —  $T_1$ ,  $T_2$  and  $T_3$

increase in the rate of collisions between molecules at higher temperature.

*Energy of activation for a reaction:* It is common knowledge that a mixture of oxygen and fuel will not burn unless a flame (match stick) is applied. Even a mixture of hydrogen and oxygen which can react in an explosive manner does not, until a spark or flame is applied. It is therefore obvious that there seems to be a barrier for these reactions to occur even though we know the direction of spontaneous change is in favour of the reaction to occur (decrease in free energy). One can draw an analogy from water in a reservoir with bunds. Even if the reservoir may be at a higher altitude than its surroundings (and hence the water is at an increased potential energy compared to what it would have outside the bund), the water cannot flow over the bund until pumped over. Arrhenius proposed that for reactants to get converted into products, there is an energy barrier, which has to be overcome. Only those encounters, in which reactants have sufficient energy, to cross this barrier, would result in products. *It is of tremendous consequence to existence of life that such energy barriers exist; otherwise, all the fuels would have been consumed by the oxygen in the air; in fact earth would not be what it is but for these barriers.*

By considering a very simple reaction, namely  $A(g) + B_2(g) \rightarrow AB(g) + B(g)$ , we can rationalise the existence of an energy of activation in the following sense. Let us consider the approach of A towards  $B_2$  along the line of the bond B-B. As A approaches B-B, the energy is nearly constant until A comes near B-B and starts pulling one of the B atoms of  $B_2$  and attains an intermediate configuration  $A \cdots B \cdots B$ . This configuration will possess a higher energy than the sum of the energies of A and  $B_2$ , since energy would have to be supplied to pull one of the B atoms from the other B atom. As A approaches closer and closer, A-B will be formed and energy will be released and let us say that the energy of AB and B is less than that of A and  $B_2$ . We can plot this energy change (Fig. 11.5) as a function of the distance between A and the B atom close to it.



The change in distance 'd' can be termed the COURSE OF THE REACTION and starts from a large value and decreases to the bond length of stable  $A - B$ .

Chemists term the arrangement of atoms corresponding to the maximum of the energy in Fig. 11.5 as an *activated complex*. The activation energy is the barrier in energy that has to be overcome before reactants convert into products. It is to be noted that for the case considered in Fig. 11.5, the activation energy for the backward reaction is higher than that for the forward reaction. As the temperature is increased the rate of both forward and backward reactions will increase, but, not by the same proportion.

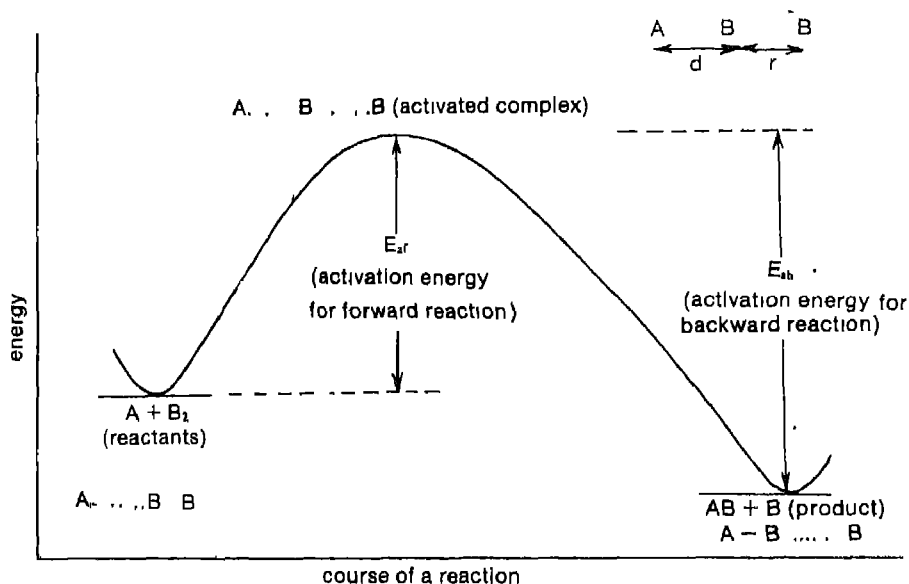


Fig. 11.5 Energy diagram for a hypothetical reaction  $A + B_2 \rightarrow AB + B$  (distance  $d$  changes for a large value to the bond length  $A-B$  with accompanying change in  $r$ )

Now we have an explanation for the inherent stability of fuels in the presence of air or oxygen and of hydrogen in the presence of oxygen. The combustion reaction has high energy of activation and hence fuels are almost inert under ordinary conditions. Once a flame is applied (such as one from a match stick) the gas near the flame is raised to a high temperature, enough for at least a portion of the fuel to burn in oxygen. The heat of combustion from the reaction of the portion of the fuel increases the temperature of the remaining gas and the flame is sustained. Very often you hear of accidents in a kitchen from a leaky cooking gas cylinder. The room is full of fuel gas and air but does not react until a person, unknowingly, strikes a match then a big fire follows. From this discussion, one realises that every reaction, feasible from consideration of free energy, need not necessarily take place, many may be prevented from occurring by a high activation energy barrier. Such reactants, though energetically (what is termed THERMODYNAMICALLY UNSTABLE) are KINETICALLY STABLE at ordinary temperature.

### 11.3.3 Catalysis

Is it possible to lower the energy of activation for reactions and hence increase the rates of reactions? That is exactly what a CATALYST does. A catalyst is a chemical species that enhances the rate of a reaction but can be recovered unchanged at the end of the reaction. (This is an ideal catalyst). It is sufficient to realise at this juncture, that what a catalyst does is to decrease the energy of activation (Fig. 11.6). We can illustrate the effect of a catalyst by the following experiments.

In two 100 cm<sup>3</sup> beakers, let us pour in 30 cm<sup>3</sup> of 0.1M oxalic acid solution and 5 cm<sup>3</sup> of dilute sulphuric acid. To one beaker we add 0.5 cm<sup>3</sup> of 0.1M MnSO<sub>4</sub> solution and to the other beaker add 0.5 cm<sup>3</sup> of water. From a dropper we add 10 drops of 0.1M potassium permanganate solution and stir the solution. The potassium permanganate decolorises faster in the beaker to which we have added MnSO<sub>4</sub>—Mn<sup>2+</sup> ions act as a catalyst

In two test tubes let us place about 0.1 g of granulated Zn. To one test tube we add 10 drops of 0.1 M copper sulphate solution. 10 cm<sup>3</sup> of 5 M hydrochloric acid is poured into each test tube at the same time and we observe the rate at which hydrogen is evolved. If possible, we can measure the hydrogen evolved by collecting it in a measuring cylinder by the method of displacement of water.

This experiment demonstrates that, while the rate of the reaction is speeded up in the presence of copper sulphate, the amount of Zn reacted (and also the amount of hydrogen produced) is the same in both the cases. The copper has remained in solution without any change.

The role of a catalyst is to take part in the reaction in such a way as to lower the energy of activation, but at the same time get released in its original chemical state at the end of the reaction (physical changes can and do occur).

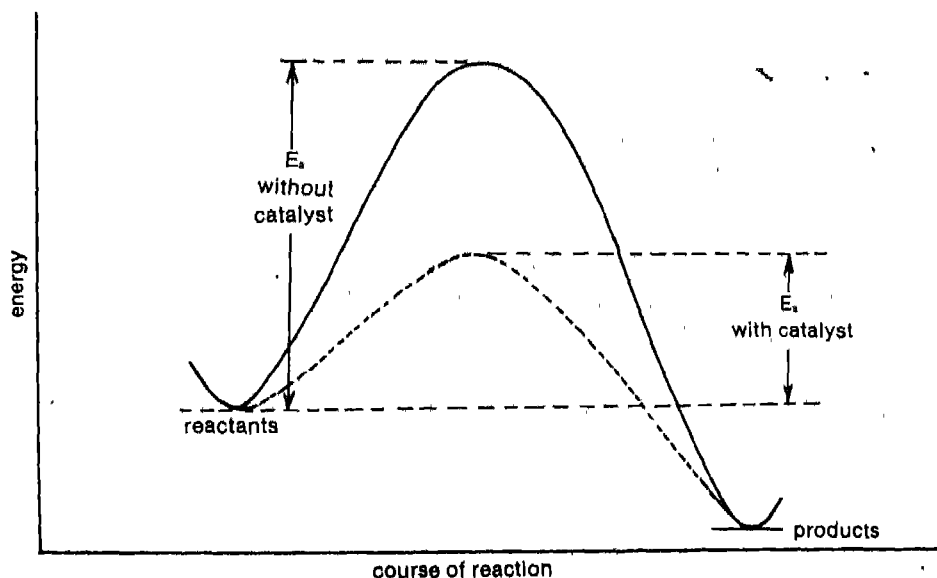
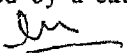


Fig. 11.6 Energy diagram for a catalysed and an uncatalysed reaction (Dotted line curve shows catalysed reaction whereas solid line curve shows uncatalysed reaction)

Catalysts are extremely important to our existence. In most industrial processes, catalysts are involved. Our entire life process depends on catalysts called ENZYMES which regulate innumerable processes that occur in a living organism. We had

mentioned earlier that it is enzymes that ensure that we derive energy for life, in many small steps, from oxidising the food we imbibe, without resort to the high temperatures, that are usually associated with the combustion of fuels.

From Fig. 11.6, it is obvious that the energy of activation is decreased by a catalyst for both forward and backward reaction. Therefore what an ideal catalyst does is to decrease the time it takes to reach an equilibrium condition. It alters the path to one which has a lower energy of activation. In other words, the extent of the completion of a reaction is *not* changed by a catalyst; what a catalyst does is to speed up the attainment of equilibrium. 

#### 11.4 EFFECT OF LIGHT ON RATES OF REACTION

In certain reactions (an outstanding example being the sequence of reactions in photosynthesis) light provides the energy to overcome the activation energy barrier. The energy absorbed may be sufficient, even to break chemical bonds and form highly reactive intermediates called *free radicals*. Some of the examples where light is used for initiating chemical reactions are:

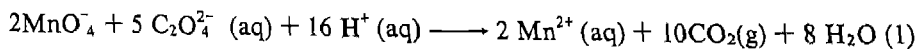
- (1) Photosynthesis
- (2) Vision (A compound, retinal, absorbs the light falling on the eye and undergoes a chemical change. This is the first step in 'seeing'.)
- (3) Photography
- (4) Blueprinting
- (5) Photochemical synthesis of compounds
- (6) Sterilisation of water (exposure of water to UV irradiation)

Blue printing can be illustrated by the following experiment:

To each of two 100 cm<sup>3</sup> beakers, we add 25 cm<sup>3</sup> of 0.02 M aqueous FeCl<sub>3</sub> solution, 20 cm<sup>3</sup> of 0.1 M oxalic acid solution in water and 5 cm<sup>3</sup> of 0.05 M potassium ferricyanide solution. One beaker is kept in the dark and the other is kept exposed to bright sunlight or to a 100 watt electric lamp. When the two solutions are compared after about half an hour it is found that the solution exposed to light has turned blue. The reaction is very similar to what occurs when blue printing is done.

#### 11.5 ELEMENTARY REACTIONS ARE STEPS TO MORE COMPLEX REACTIONS

Since reactants have to encounter with sufficient energy for a reaction to occur, the probability of such an event decreases drastically as the number of participants in a reactive encounter increases. Thus the possibility of three molecules involved in a reaction is much smaller than those involving two. Thus we write a stoichiometric equation:



It is obvious that the reaction does not proceed at one step in the manner written above. The probability for 23 species to get together and yield 20 species is very much smaller than the reciprocal of the life of the universe. Therefore stoichiometric equations in chemical arithmetic only tell us what the overall reactions are. They

tell us nothing about how such a reaction will proceed—what the steps involved are. These have to be inferred from many experiments.

For the present, it is sufficient to realise that most chemical reactions involve many intermediate steps called elementary reactions involving one, two or a maximum of three species. The overall rate of a reaction (i.e., the rate of production of final products) will be determined by the rate of the slowest step. Fig 11.7 draws an analogy between a series of tubes of different diameters and a reaction involving a few intermediate steps with different rates

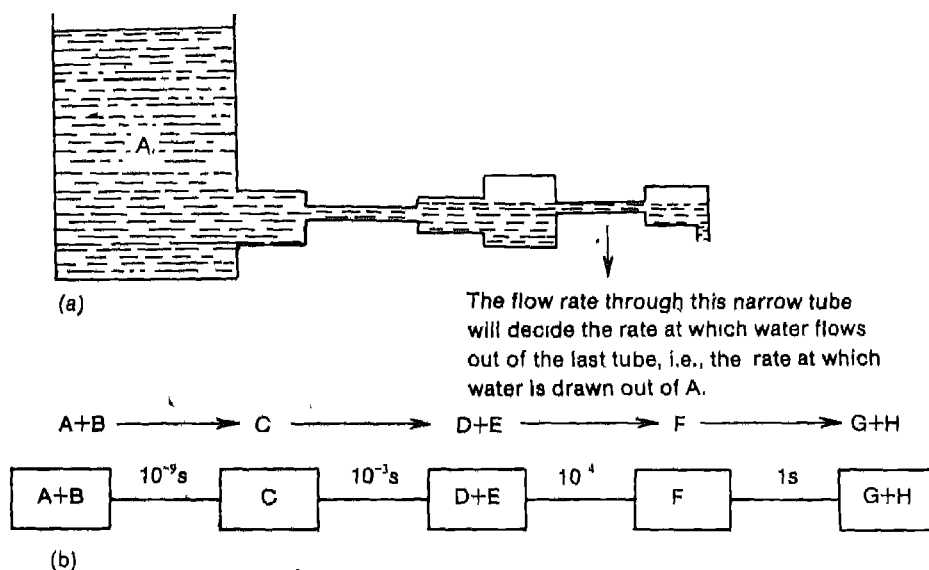


Fig. 11.7 Overall rate of reaction is governed by the rate of slowest intermediate step(s). (The rate of formation of G and H will be decided by the slowest step, that is D + E  $\rightarrow$  F, which has a life time of 1s)

In such cases the initial rate of disappearance of reactants is not usually the same as the rate of formation of products. The narrowest pipe and the slowest step act as 'bottlenecks'.

## 11.6 HOW FAST ARE CHEMICAL REACTIONS ?

The rates of chemical reactions vary from the slowest with reaction times of the order of millions of years to the fastest with reaction times of the order of  $10^{-12}$  seconds. Modern techniques, mainly using lasers, are now available to study extremely fast reactions. Time at the shortest scales are indicated as:

$10^{-3}s$	=	1 millisecond
$10^{-6}s$	=	1 microsecond
$10^{-9}s$	=	1 nanosecond

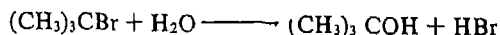
$$\begin{aligned}
 10^{-12}\text{s} &= 1 \text{ picosecond} \\
 10^{-15}\text{s} &= 1 \text{ femtosecond}
 \end{aligned}$$

The range of reaction times observed cover as many as 26 orders of magnitude 1 picosecond =  $10^{-12}$  second to 1 million years =  $3 \times 10^{13}$  seconds. Some examples are listed below.

Reaction		Reaction times (half lives)
1.	First step in photosynthesis Chlorophyll <u>light</u> excited chlorophyll $\longrightarrow$ electron transfer to another molecule	$10^{-12}\text{s}$
2	First step in vision (Retinal isomerisation)	$10^{-12}\text{s}$
3	$\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{H}_2\text{O}$	$10^{-10}\text{s}$
4.	$\text{NO}_2(\text{g}) + \text{NO}_2(\text{g}) \longrightarrow \text{N}_2\text{O}_4(\text{g})$	$10^{-6}\text{s}$
5	$\text{Fe}^{3+} + \text{SCN}^- \longrightarrow \text{Fe}(\text{SCN})^{2+}$	$5 \times 10^{-13}\text{s}$
6	$\text{H}_2\text{CO}_3(\text{aq}) \longrightarrow \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$	60 s
7	$\text{N}_2\text{O}_5 \longrightarrow 2 \text{NO}_2 + \frac{1}{2} \text{O}_2$ (at $55^\circ\text{C}$ )	89 min
8	Sucrose + Water $\longrightarrow$ Glucose + Fructose	200 min
9	$\text{Cr}(\text{H}_2\text{O})_6^{3+}(\text{aq}) + \text{F}^-(\text{aq}) \longrightarrow \text{Cr}(\text{H}_2\text{O})_5\text{F}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	1000 hrs
10	$\text{CH}_3\text{COOC}_6\text{H}_5(\text{aq}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{CH}_3\text{COOH}(\text{aq}) + \text{C}_6\text{H}_5\text{OH}(\text{aq})$	1000 days
11.	$\text{Cr}(\text{H}_2\text{O})_6^{3+}(\text{aq}) + \text{I}^-(\text{aq}) \longrightarrow \text{Cr}(\text{H}_2\text{O})_5\text{I}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	2000 years

### EXERCISES

- 11.1 Given the following data plot the concentration of reactant (tert. butyl bromide) and the product (tert butyl alcohol) as a function of time in an acetone—water mixture at 323 K



Time (min)	Concentration of $(\text{CH}_3)_3\text{CBr}$ (mol $\text{L}^{-1}$ )	Concentration of $(\text{CH}_3)_3\text{COH}$ (mol $\text{L}^{-1}$ )
0.00	0.106	0
10	0.095	0.011
20	0.085	0.020
30	0.074	0.033
40	0.065	0.040
50	0.058	0.048
60	0.050	0.056



Time (min)	Concentration of $(\text{CH}_3)_3\text{CBr}$ (mol L <sup>-1</sup> )	Concentration of $(\text{CH}_3)_3\text{COH}$ (mol L <sup>-1</sup> )
80	0.038	0.069
100	0.029	0.076
120	0.021	0.085
140	0.017	0.087

Plot the concentration of the two species as a function of time.

- Find out the instantaneous rates of disappearance of tert. butyl bromide and the rate of appearance of tert. butyl alcohol at  $t = 20, 40, 80, 100$  min. Verify that the two rates are equal (within limits of your measurements) Also determine the average rates at these times.
- Find out the average rate of reaction for 0 to 10%, 20 to 40%, 50 to 60%, 80 to 90% reaction

11.2 For the reaction  $2\text{A} + \text{B} \longrightarrow \text{C}$  the following were collected:

Expt No	Initial Concentration		Initial Rate of Formation of C mol L <sup>-1</sup> s <sup>-1</sup>
	A mol L <sup>-1</sup>	B mol L <sup>-1</sup>	
1	0.10	0.200	$3 \times 10^2$
2	0.30	0.40	$3.6 \times 10^3$
3	0.30	0.80	$1.44 \times 10^4$
4	0.20	0.40	?
5	0.10	0.40	?

Find out how the rate of the reaction depends upon the concentration of [A] and [B] and fill in the blanks.

11.3 Explain the following

- Average rate
- life time and half life time
- rate constant
- reaction order

11.4 Explain why

- powdered sugar dissolves faster than crystalline sugar,
- it takes more time to boil an egg or cook rice at higher altitudes,
- we save our fuel when we use a pressure cooker for cooking rice, potatoes, meat, etc.,
- there is no difference in cooking time between sea-level and higher altitudes when we use a pressure cooker at both places.

11.5 Identify, giving reasons, the faster reaction in each of the reaction pairs

- $\text{Na(s)} + \text{I}_2(\text{s}) \longrightarrow 2 \text{NaI(s)}$   
 $\text{Na(s)} + \text{I}_2(\text{g}) \longrightarrow 2 \text{NaI(s)}$  *faster*
- $\text{C(s)} + \text{H}_2\text{O(g)} \longrightarrow 2 \text{H}_2(\text{g}) + \text{CO}_2(\text{g})$   
 $\text{C(s)} + \text{H}_2\text{O(s)} \xrightarrow{\text{Catalyst}} 2 \text{H}_2(\text{g}) + \text{CO}_2(\text{g})$  *faster*
- $\text{C(s)} + \frac{1}{2} \text{O}_2(\text{g}) \xrightarrow{500^\circ\text{C}} \text{CO(g)}$   
 $\text{C(s)} + \frac{1}{2} \text{O}_2(\text{g}) \xrightarrow{1000^\circ\text{C}} \text{CO(g)}$  *faster*
- $\text{N}_2(10 \text{ atm}) + 3 \text{H}_2(10 \text{ atm}) \longrightarrow 2 \text{NH}_3(\text{g})$   
 $\text{N}_2(5 \text{ atm}) + 3 \text{H}_2(5 \text{ atm}) \longrightarrow 2 \text{NH}_3(\text{g})$  *faster*

11.6 Calculate the change in surface area when spherical particles of 0.1 mm diameter are ground to spherical particles of 0.025 mm diameter (for the same volume)

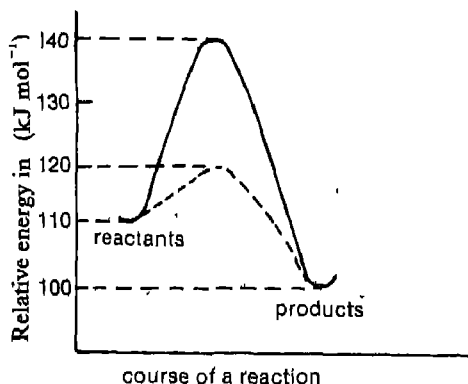
11.7 Explain the following:

- A lump of coal burns at a moderate rate in air while coal dust burns explosively.
- Liquid bromine reacts slowly as compared to bromine vapour.

11.8 Which of the following statements is true?

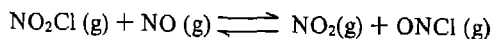
- Endothermic reactions have higher activation energies than exothermic reactions.
- While the extent of an exothermic reaction will decrease with increase of temperature, rate of reaction will increase.
- The rate of a catalysed reaction is independent of the concentration of the catalyst.

11.9 Given the following picture



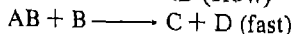
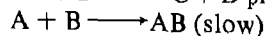
- Calculate  $\Delta H$  for the reaction and energy of activation for the forward reaction and energy of activation for the backward reaction.
- The dotted curve is in the presence of a catalyst. What is the energy of activation for the two reactions in the presence of the catalyst?
- Will the catalyst change the extent of the reaction?

11.10 The reaction:



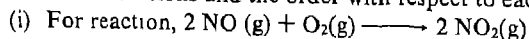
is a single step reversible reaction. The energy of activation for forward reaction,  $E_{af}$  is 28.9 kJ and that for backward reaction,  $E_{ab}$  is 41.8 kJ. Draw an energy diagram for the reaction. Indicate  $E_{af}$  and  $E_{ab}$  and  $\Delta H$  of the diagram.

11.11 If the reaction  $\text{A} + 2\text{B} \longrightarrow \text{C} + \text{D}$  proceeds in 2 steps

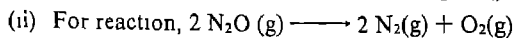


which one of the two steps determines the rate of formation of products?

11.12 With the help of the following rate expressions of the reactions, find out the overall order of the reactions and the order with respect to each reactant:



$$\text{rate} = k [\text{NO}_2]^2 [\text{O}_2]$$



$$\text{rate} = k [\text{N}_2\text{O}]$$

(iii) For reaction,  $2 \text{NO}_2(\text{g}) \longrightarrow 2 \text{NO}(\text{g}) + \text{O}_2(\text{g})$

$$\text{rate} = k [\text{NO}_2]^2$$

(iv) For reaction,  $2\text{NO}(\text{g}) + 2\text{H}_2(\text{g}) \longrightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$

$$\text{rate} = k [\text{NO}]^2 [\text{H}_2]$$

(v) For reaction,  $\text{SO}_2\text{Cl}_2(\text{g}) \longrightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$

$$\text{rate} = k [\text{SO}_2\text{Cl}_2]$$

11 13 Explain and illustrate the following:

- (i) Average rate of a reaction
- (ii) Thermodynamic and kinetic stability
- (iii) Activated complex.

## UNIT 12

### CHEMISTRY OF NON-METALS—I (Hydrogen, Oxygen and Nitrogen)

*Hydrogen, oxygen and nitrogen—  
are elements essential for the  
sustenance of life.*

1																18
H	2															

#### OBJECTIVES

In this Unit, we shall learn

- \* the chemistry of hydrogen and hydrides of elements;
- \* the chemistry of oxygen and some oxides;
- \* the chemistry of ozone, water and hydrogen peroxide;
- \* the chemistry of nitrogen;
- \* the manufacture, properties and uses of ammonia and nitric acid.

IN UNITS 4 AND 5, we learnt how the electronic configuration of elements determines their physical and chemical properties. We also learnt how the electronic structure provides a basis for classifying elements into various groups or families. In this and subsequent Units, we shall briefly survey the chemistry of a few selected elements and their important compounds. We shall specially study their applications in everyday life.

Metals constitute a majority of all known elements ( $>75\%$ ) and appear on the left-hand side of the periodic table (Fig. 12.1). In general they have low electronegativities (tendency to attract electrons). Typical non-metals are found on the right-hand side of the periodic table (Fig 12 1). Non-metals, except for the noble gases, have high electronegativities. This division of elements into metals and non-metals is somewhat arbitrary. There are elements which lie on the border-line between metals and non-metals and show intermediate properties

1								18
H	2		13	14	15	16	17	He
Li	Be		B	C	N	O	F	Ne
Na	Mg		Al	Si	P	S	Cl	Ar
K	Ca		Ga	Ge	As	Se	Br	Kr
Rb	Sr		In	Sn	Sb	Te	I	Xe
Cs	Ba		Tl	Pb	Bi	Po	At	Rn
Fr	Ra							

d- and f - block  
elements

Fig. 12.1 Representative elements and noble gases (Diagram shows the separation of metals and non-metals. Group numbers are shown at the top of each column. Non-metals are shown in colour. The elements in the shaded squares are called Metalloids and many of them become metallic when they are melted)

This Unit is devoted to the chemistry of three typical non-metals: hydrogen, oxygen and nitrogen. The chemistry of carbon has already been discussed earlier in Unit 7.

## 12.1 HYDROGEN

### 12.1.1 Position in the Periodic Table

The position of hydrogen in the periodic table is debatable. Because hydrogen has only one electron ( $1s^1$ ), it may be grouped with the alkali metals. It can also be placed in the company of the halogens, because like the halogens, it needs one electron to attain the stable noble gas configuration. Although hydrogen shows similarities in its chemical behaviour to both alkali metals and halogens, it differs from them in many ways.

Hydrogen resembles the alkali metals in its ability to form hydrated unipositive ion [ $H^+(aq)$ ]. But the ionisation energy of hydrogen ( $1312 \text{ kJ mol}^{-1}$ ) is very high compared to the alkali metals. In its high ionisation energy, hydrogen resembles the halogens and forms numerous covalent compounds. The simplest of these covalent species is the diatomic  $H_2$  molecule itself which we shall refer to as dihydrogen to distinguish it from the hydrogen atom. Dihydrogen molecule is very stable and dissociates to an appreciable extent only at very high temperatures ( $>2000 \text{ K}$ ). Atomic and molecular properties of hydrogen are summarised in Table 12.1.

TABLE 12.1

Atomic and Molecular Properties of Hydrogen

Atomic Properties		Molecular Properties	
Ionisation energy ( $\text{kJ mol}^{-1}$ )	1310	Melting point (K)	13.8
Electron affinity ( $\text{kJ mol}^{-1}$ )	72.8	Boiling point (K)	20.4
Electronegativity	2.1	Density ( $\text{g/cm}^3$ )	0.0899
Atomic radius (pm)	37	Bond length (pm)	74.2
Ionic radius ( $H^+$ ) (pm)	210	Bond energy ( $\text{kJ mol}^{-1}$ )	435.9

### 12.1.2 Occurrence

Hydrogen is the most abundant element in the universe. The giant planets Jupiter and Saturn consist mostly of hydrogen. About half the mass of the sun and the stars is accounted for by hydrogen.

On the earth, hydrogen is present in water, coal, petroleum, clay and in all animal and vegetable matter. It constitutes 0.9% by weight of the earth's crust and is the ninth element in order of abundance. The source of the sun's energy, which is necessary for life on earth, is the fusion of hydrogen nuclei to form helium.

### 12.1.3 Isotopes of Hydrogen

There are three isotopes of hydrogen with mass numbers 1, 2 and 3 and their natural abundances are in the ratio  $1.156 \times 10^{-2} : 1 \times 10^{-17}$ . The isotope with mass number 2 is called DEUTERIUM ( $^2H$  or D) or HEAVY HYDROGEN, the isotope with mass number 3 is called TRITIUM ( $^3H$  or T). Of these, tritium is radioactive. Because

isotopes of an element have the same electronic configurations, they exhibit the same chemical behaviour. But, because of their different masses, they differ in their physical properties and also in the rates of their reactions. In general, ordinary hydrogen undergoes reactions more rapidly than deuterium. Some physical constants for  $H_2$  and  $D_2$  are given in Table 12.2.

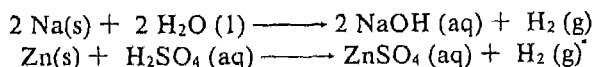
TABLE 12.2  
Comparison of the Physical Properties of Dihydrogen ( $H_2$ ) and its Deuterium Analogue ( $D_2$ ).

Property	$H_2$	$D_2$
Molecular mass	2.016	4.028
Melting point (K)	13.8	18.7
Boiling point (K)	20.4	23.9
Heat of fusion ( $\text{kJ mol}^{-1}$ )	0.117	0.197
Heat of vapourisation ( $\text{kJ mol}^{-1}$ )	0.904	1.226
Bond energy ( $\text{kJ mol}^{-1}$ ) (298.2 K)	435.9	443.4

Deuterium is usually prepared from HEAVY WATER ( $D_2O$ ) which is manufactured by the electrolytic enrichment of ordinary water. Heavy water is used as a coolant and moderator in nuclear reactors. Heavy water is manufactured in our country in Bārōda, (Gujarat), Kōzī, Rājasthān, Muticorin (Tamil Nadu) and Thal (Maharashtra).

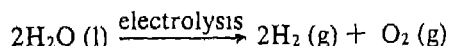
#### 12.1.4 Preparation of Dihydrogen

Dihydrogen can be prepared by the action of water or dilute mineral acids on metals.

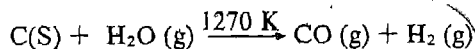
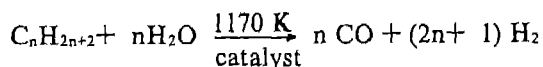


A convenient laboratory method of preparation of dihydrogen is the treatment of zinc granules with dilute hydrochloric or sulphuric acid. This type of reaction is known as a DISPLACEMENT REACTION. Metals above hydrogen in the ELECTRO-MOTIVE SERIES can displace hydrogen from acids (see Unit 10).

Dihydrogen of high purity is usually obtained by the electrolysis of water in the presence of a small amount of base or acid. This method is, however, quite expensive.



Industrially, dihydrogen is produced by the action of steam on hydrocarbons (steam reforming of hydrocarbons) or by the action of steam on coke at a high temperature.



The mixture of dihydrogen and carbon monoxide is known as WATER GAS.

Dihydrogen is also produced as a by-product in the manufacture of sodium hydroxide (NaOH) by the electrolysis of sodium chloride (NaCl).

### 12.1.5 Properties and Reaction of Dihydrogen

Dihydrogen is a colourless, tasteless, odourless gas with a very low solubility in water. It is inflammable and should be handled with care.

Under appropriate experimental conditions, hydrogen forms compounds with almost all elements except the noble gases. Hydrogen forms more compounds than any other element.

Because of its high bond dissociation energy ( $436 \text{ kJ mol}^{-1}$ ), dihydrogen is not particularly reactive. At elevated temperatures or in the presence of catalysts, it combines with many non-metals to form covalent hydrides. With reactive metals (e.g., alkali metals) it forms salt-like hydrides, in which its oxidation number is  $-1$ . A few typical reactions of dihydrogen are summarised in Fig. 12.2. In addition to

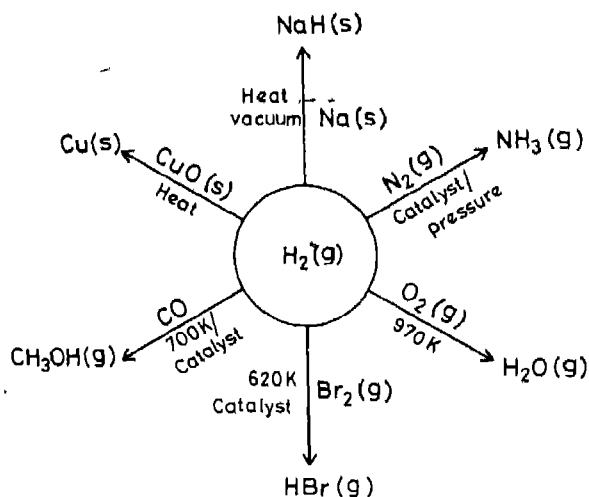


Fig. 12.2 Some typical reactions of dihydrogen

covalent and salt-like hydrides, with metals such as platinum, palladium and nickel, dihydrogen forms INTERSTITIAL HYDRIDES in which hydrogen atoms, because of their small size, occupy interstitial holes in the metallic crystal.

### 12.1.6 Uses of Dihydrogen

The largest industrial use of dihydrogen is in the manufacture of ammonia by direct union with nitrogen (Haber's process; Section 9.3.1). Large quantities of hydrogen are also used in the hydrogenation of unsaturated vegetable oils to give solid fats (e.g., vanaspathi) and for the production of organic chemicals (e.g., methanol by the

reaction  $\text{CO} + 2\text{H}_2 \xrightarrow[\text{Catalyst}]{\text{Cobalt}} \text{CH}_3\text{OH}$ ). Other uses of hydrogen include the production of HCl and the reduction of oxides to metals in metallurgy. It is used in oxy-



### HYDROGEN—A FUTURE FUEL?

Saturn V, the rocket that launched Neil Armstrong to the moon, was powered by liquid hydrogen fuel. Oxygen (needed for combustion) as well as hydrogen were carried by the rocket in separate tanks.

The property of high flammability should favour the use of hydrogen as a fuel. However, its use is limited due to the lack of availability of free hydrogen in nature. Another difficulty is safe storage and distribution of this explosive fuel.

A widely available source of hydrogen is water but a lot of energy has to be expended to release the hydrogen from water. For economising on fuel expenses, methods of tapping cheap sources of energy like solar energy are being tested. A day may come when hydrogen could be supplied by pipelines for domestic use. By carrying it in the liquid form in storage tanks it may also be used in vehicles. An alternative method would be to carry a solid metal hydride that decomposes on heating to give the metal and hydrogen.

hydrogen torch for welding and in the liquid form as a rocket fuel in space programmes.

Hydrogen is also considered to be a source of energy for use in industry and transportation. If such a 'hydrogen economy' becomes a reality, it could solve some of the problems of the present-day energy crisis.

#### 12.2 OXYGEN

The electronic configuration of oxygen in its ground state is  $1s^2 2s^2 2p^4$ . There are three naturally occurring isotopes of oxygen,  $^{16}\text{O}$  (99.76%),  $^{17}\text{O}$  (0.037%) and  $^{18}\text{O}$  (0.204%). Like hydrogen, oxygen exists in the elemental form as a diatomic molecule ( $\text{O}_2$ ). Dioxygen ( $\text{O}_2$ ) is unique among diatomic molecules. It contains an even number of electrons (16) but two of them are unpaired. Dioxygen is therefore paramagnetic (see Unit 6). The properties of atomic and molecular oxygen are given in Table 12.3.

TABLE 12.3

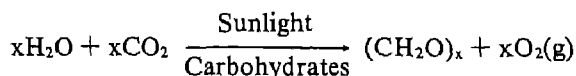
Atomic and Molecular Properties of Oxygen

Atomic Properties		Molecular Properties	
Ionisation energy ( $\text{kJ mol}^{-1}$ )	1310	Melting point (K)	54.4
Electron affinity ( $\text{kJ mol}^{-1}$ )	140	Boiling point (K)	90.2
Electronegativity	3.5	Density ( $\text{g/cm}^3$ ) at STP	1.429
Atomic radius (pm)	73	Bond length (pm)	120.7
Ionic radius ( $\text{O}^{2-}$ ) (pm)	140	Bond energy ( $\text{kJ mol}^{-1}$ )	493.4

### 12.2.1 Occurrence

Just as hydrogen is the most abundant element in the cosmos, oxygen is the most abundant element on earth. Oxygen constitutes nearly 50% by weight of the crust of the earth, bodies of water and the atmosphere. In the earth's crust, oxygen occurs in the combined state, mainly in the form of silicates, carbonates and oxides of metals. Water consists of 88.8% oxygen by weight. Dioxygen makes up about 23.2% by weight of the atmosphere.

Almost all of the dioxygen in the atmosphere is believed to be the result of photosynthesis by green plants. Photosynthesis is quite a complicated process, but for simplicity, it can be represented by the equation



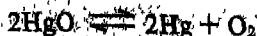
### PHLOGISTON THEORY AND THE DISCOVERY OF OXYGEN

In the eighteenth century, it was universally accepted by all chemists that all substances that burn, do so because they contain a substance called PHLOGISTON, which is released during combustion. If this view is correct, then combustion should lead to a decrease in weight.

In August 1774, Joseph Priestley heated red mercuric oxide by focussing the sun's rays on it with the help of a biconvex lens. Liquid metallic mercury and a colourless gas were obtained. The gas was observed to help a candle to burn more brightly than in air; it was named 'dephlogistised air.'

The phlogiston theory was investigated by Lavoisier by reversing the method followed by Priestley. He heated mercury in a sealed air-filled flask in a furnace. It was only on the second day that the reaction was visible in the form of red specks on the surface of the metallic mercury. After twelve days, Lavoisier removed the flask and weighed its contents. To his surprise the mass of mercury had increased. This definitely proved the phlogiston theory to be wrong.

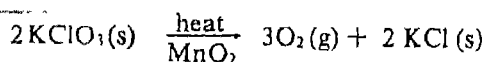
Lavoisier obtained a liquid metal and a colourless gas on heating the red specks; the colourless gas helped to support combustion better than air. Since this gas could not be decomposed further, he concluded that it must be an element and named it oxygen. Thus the reaction equation is written as



### 12.2.2 Preparation

In the laboratory, dioxygen is obtained by the thermal decomposition of oxygen-rich compounds such as  $\text{KMnO}_4$  or  $\text{KClO}_3$ . The thermal decomposition of  $\text{KClO}_3$

requires a temperature of 670-720 K. The temperature can be lowered to ~420 K by the use of  $\text{MnO}_2$  as a catalyst.



✓ Another way to prepare dioxygen in the laboratory is by the reaction of water on sodium peroxide:



Electrolysis of water produces both dihydrogen and dioxygen in a pure state. The most economical method of production of dioxygen on an industrial scale is the fractional distillation of liquid air. In this method, dinitrogen (b.p. 77 K) is boiled away leaving behind dioxygen (b.p. 90 K). Production of dioxygen in the world is more than 100 million tonnes per year.

### 12.2.3 Properties and Reactions

Dioxygen is a colourless, tasteless and odourless gas. Its solubility in one litre of water at 293 K is ~ 30 cm<sup>3</sup> gas at STP. This small amount of dissolved dioxygen is sufficient to sustain marine and aquatic life and for the destruction of organic wastes in water bodies.

Dioxygen combines with many metals and non-metals to form binary compounds of oxygen known as OXIDES. The bond dissociation energy of  $\text{O}_2$  is high (comparable to that of  $\text{H}_2$ ) and hence the reactions of dioxygen require initiation by external heating. Many of these reactions are highly exothermic and the heat liberated is sufficient to sustain the reactions (e.g., combustion of charcoal). Most metals (except some of the less active ones such as gold and platinum) and most non-metals (with the exception of noble gases) react with dioxygen directly. Some typical reactions of dioxygen are summarised in Fig 12.3.

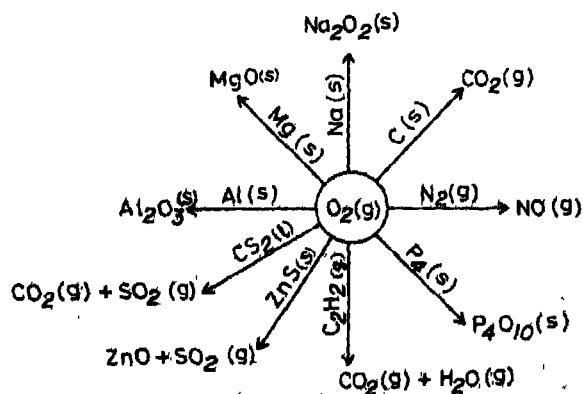


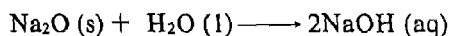
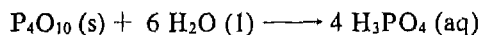
Fig. 12.3 Some typical reactions of dioxygen

### 12.2.4. Uses of Dioxygen

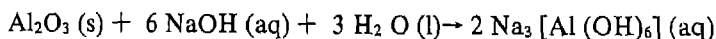
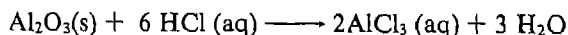
One of the major uses of dioxygen is in making steel and in metal fabrication where it functions as an aid to combustion. Another important use is in the production of oxygen-containing organic chemicals (e.g., ethylene oxide from ethene). Dioxygen is essential for life support systems (e.g., in hospitals, in underwater diving). Liquid dioxygen is used as an oxidiser in rockets for space exploration and in the launching of satellites.

### 12.2.5 Simple Oxides

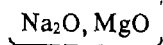
As mentioned earlier, oxygen forms compounds with most elements of the periodic table. Many elements form more than one compound with oxygen. In their properties and with regard to nature of bonding, they vary widely. They form both ionic and covalent compounds. A useful classification of the oxides is based on *acid-base characteristics*. An oxide that combines with water to give an acid is termed as an ACIDIC OXIDE, an oxide that gives a base in water is known as a BASIC OXIDE. An example for each type of oxide is shown below.



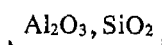
As a general rule, non-metal oxides are acidic whilst metal oxides are basic. Some oxides are of an intermediate nature, they react with both acids and alkalies and are called AMPHOTERIC OXIDES. These are generally formed by elements that are on the borderline between metals and non-metals (located in the centre of the periodic table).



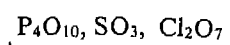
It may be noted that when we consider the oxides of elements in a given period, there is a progression from strongly basic through amphoteric to strongly acidic oxides.



Basic



Amphoteric



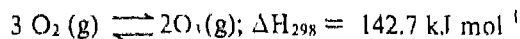
Acidic

Undoubtedly, the most important among the simple oxides is water, whose chemistry will be discussed later in this Unit.

### 12.2.6 Ozone

In addition to the diatomic molecule,  $\text{O}_2$ , elemental oxygen exists as a triatomic species,  $\text{O}_3$ , known as ozone. The existence of an element in more than one modification in the same physical state is referred to as ALLOTROPY.

Ozone is a pale blue gas with a characteristic pungent odour. It condenses to a deep blue liquid (b.p. 161.2 K) and to a violet-black solid (m.p. 80.6 K). Ozone is formed when energy is supplied to dioxygen in the form of UV radiation or silent electric discharge.



The ozone molecule has an angular structure (Fig. 12.4a). Both the oxygen-oxygen bonds are of equal length (128 pm). This distance is intermediate between that of a O-O single bond (148 pm) and that of a O=O double bond (110 pm). The bonding in ozone is best described as a resonance hybrid as shown below.

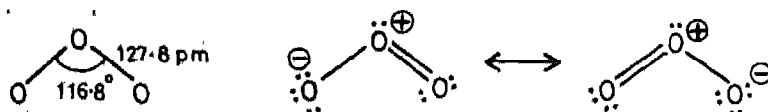
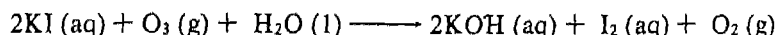
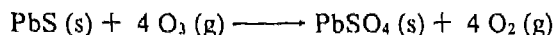


Fig. 12.4 (a) Geometry of the ozone molecule (b) valence bond description of bonding in ozone

In contrast to dioxygen which is paramagnetic, ozone is diamagnetic. Ozone is much more reactive than dioxygen. It acts as a powerful oxidising agent with the liberation of dioxygen. Two typical reactions are.



The oxidation of potassium iodide by ozone can be conveniently used for the estimation of ozone.

Ozone is formed in the upper atmosphere by a photochemical reaction involving dioxygen. Ozone absorbs radiation strongly in the ultraviolet region of the spectrum between 220-290 nm and this protects the earth and its inhabitants from the harmful ultraviolet radiation of the sun. Without this protective layer, more ultraviolet radiation will reach the surface of the earth and cause damage to plant and animal life.

Ozone is used as a disinfectant (purifying drinking water) and as a bleaching agent. It also finds use as a chemical reagent in organic chemistry.

### 12.3. WATER AND HYDROGEN PEROXIDE

Water is a highly interesting and unique substance from a chemical point of view. Water is essential to all forms of life. It is the most abundant compound in the biosphere. Of the total estimated global water supply of  $\sim 1.4 \times 10^9 \text{ km}^3$ , the oceans and inland saline water bodies hold 97.3% and fresh water amounts to only 2.7%. Unfortunately most of the fresh water is not readily accessible, being locked up in frozen lakes, glaciers or under the ground. The fraction of water available for human use is only 0.003% of the total global water supply.

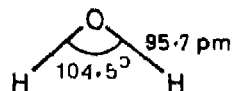
In nature, water is found in all three phases—solid, liquid and gas. An important milestone in the development of modern chemistry is Cavendish's experiments in the

second half of the eighteenth century which established the composition of water as consisting of two parts of hydrogen and one part of oxygen.

Apart from water, hydrogen and oxygen form another oxide, hydrogen peroxide, which has the molecular formula  $\text{H}_2\text{O}_2$ . It was discovered by Lthenard in 1918. It is formed in trace quantities by the action of sunlight on water containing dissolved oxygen. In its chemical properties, hydrogen peroxide is very different from water

### 12.3.1 Structure of Water Molecule and its Aggregates

A molecule of water consists of two hydrogen atoms joined to an oxygen atom by covalent bonds. The molecular dimensions in the gas phase are shown



There are two lone pairs of electrons on the oxygen atom. Because of the high electronegativity of oxygen (second only to fluorine), water molecule is highly polar, the oxygen atom has a partial negative charge and the hydrogen atoms have partial positive charges as shown

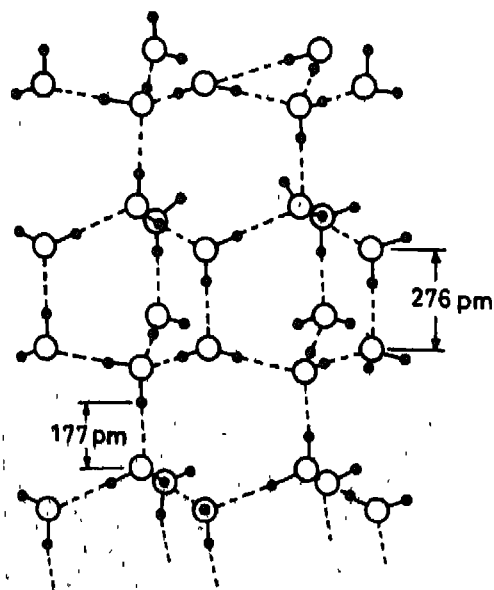
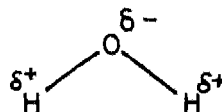


Fig. 12.5 Structure of normal hexagonal ice (The dotted lines represent hydrogen bonds. There is one hydrogen along each oxygen-oxygen axis closer to one of the two oxygen atoms)

In liquid water, water molecules are held together by hydrogen bonds (Unit 6). Each oxygen can form two hydrogen bonds utilising each of two lone pairs. Many of the curious properties of water compared with those of the hydrides of other group-16 elements (e.g.,  $\text{H}_2\text{S}$ ) arise as a result of HYDROGEN BONDING. We have still to learn much about the structure of liquid water. Experimental studies suggest that liquid water consists of aggregates of varying number of water molecules held together by hydrogen bonds and 'free' water molecules in a dynamic equilibrium with the aggregate continually forming, collapsing and reforming.

Ice, the solid form of water, can exist in different crystalline forms depending on the conditions employed for freezing the water. In the 'normal' hexagonal ice, each

oxygen atom is tetrahedrally surrounded by four other oxygen atoms, there being a hydrogen bond between each oxygen atom and two other oxygen atoms. Such an arrangement leads to a packing with a lower density than that of liquid water. When the hydrogen bonds are broken and the water molecules become more closely packed. As a result, there is an increase in density above the melting point (273 K).

As the temperature increases, the density increases gradually reaching a maximum at 277 K. Thereafter, increasing thermal motion of the molecules becomes more prominent and the density decreases with temperature as found for most liquids. Because of its lower density compared with liquid water, ice floats on water. This enables the freezing of the underlying water enabling life to survive in cold climates.

### 12.3.2 Physical Properties of Water

Many of the peculiar properties of water can be traced to the presence of hydrogen bonds in its condensed phases. Some properties of liquid water ( $\text{H}_2\text{O}$ ) and its deuterium analogue heavy water ( $\text{D}_2\text{O}$ ) are summarised in Table 12.4. The abnormally high freezing point, boiling point, heat of vaporisation and heat of fusion (compared to the hydrides of other elements of the same group of the periodic table e.g.,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$ ) arise from the presence of hydrogen bonds. Water has a higher specific heat, thermal conductivity and surface tension than most other liquids. These properties are responsible for water to play a vital role in the biosphere. The high heat of vaporisation and the high heat capacity of water are responsible for

TABLE 12.4

Some Physical Properties of Water and Heavy Water at 298 K

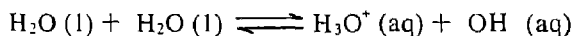
	$\text{H}_2\text{O}$	$\text{D}_2\text{O}$
Molecular Weight	18.015	20.028
Melting Point (K)	273.2	276.8
Boiling Point (K)	373.2	374.4
Temperature of Maximum Density	277.1	284.4
Maximum Density ( $\text{g cm}^{-3}$ )	1.000	1.106
Density ( $\text{g cm}^{-3}$ )	0.997	1.104
Heat of Vaporisation (373 K) ( $\text{kJ mol}^{-1}$ )	40.66	41.61
Heat of Fusion ( $\text{kJ mol}^{-1}$ )	6.01	6.28
Specific Heat ( $\text{J g}^{-1}\text{K}^{-1}$ )	4.177	—
Ionisation Constant, $[\text{H}^+][\text{OH}^-]$ ( $\text{mol}^2 \text{L}^{-2}$ )	$1.008 \times 10^{-14}$	$1.95 \times 10^{-15}$
Heat of formation, $\Delta H_f$ ( $\text{kJ mol}^{-1}$ )	-285.9	-294.6

the moderating influence of water on the climate and body temperature of living organisms. ~~Water is also an excellent solvent for transporting ions and molecules needed by plant and animal metabolism.~~ Even covalent organic compounds such as alcohols and carbohydrates have a high solubility in water because of their ability to form hydrogen bonds with water molecules.

### 12.3.3 Chemical Properties of Water

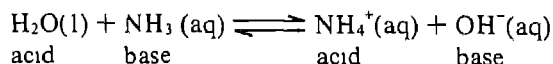
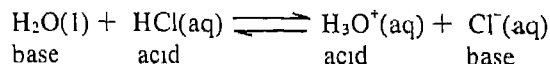
Water displays a versatile range of chemical behaviour. It acts as an acid, a base, an oxidant, a reductant and as a ligand to metal ions. Water molecule exhibits a high thermal stability as would be anticipated from its high negative heat of formation (Table 12.4). Appreciable decomposition of water to the elements requires high temperatures. The extent of dissociation at 1500 K is  $< 0.02\%$ .

Pure water has a small but measurable electrical conductivity because of the following equilibrium



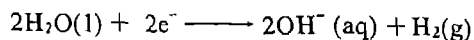
$$K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2} \text{ at } 298 \text{ K}$$

Thus water can act both as an acid and a base, and is said to be AMPHOTERIC. Water acts as a base towards acids stronger than itself and as an acid in the presence of a base stronger than itself, as shown below



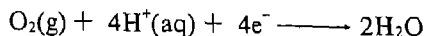
The autoprotolysis of water is thus of great importance in acid-base chemistry (Unit 9).

Apart from acid-base reactions, another class of reactions of importance in aqueous chemistry comprises the OXIDATION-REDUCTION reactions (Unit 10). Water is reduced to  $\text{H}_2$  by metals for which  $E^\circ$  value of the redox couple  $\text{M}^{n+}/\text{M}$  is below  $-0.41 \text{ V}$



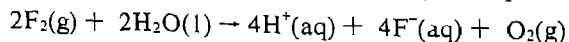
$$E^\circ = -0.41 \text{ V for } [\text{OH}^-] = 10^{-7} \text{ M}$$

Water can also be oxidised as represented by the equation.



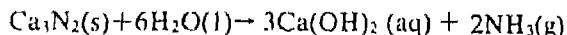
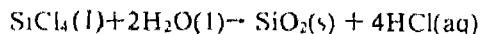
$$E^\circ = +0.82 \text{ V for } [\text{H}^+] = 10^{-7} \text{ M}$$

Typical examples of this type of reaction are oxidation of water to  $\text{O}_2$  during photosynthesis and oxidation by fluorine represented by the equation:



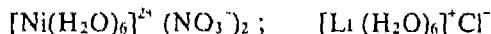


Water can participate in many HYDROLYSIS reactions as shown below



Water also has the ability to form compounds with some metal salts known as HYDRATES. Three categories of hydrates can be recognised:

(a) Water molecules are coordinated to a metal ion in complex ions as shown below

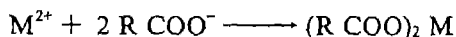


(b) Water molecules may be hydrogen bonded to certain oxygen containing anions. An interesting example is  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , in which four water molecules are coordinated to a central  $\text{Cu}^{2+}$  ion while the fifth water molecule is hydrogen bonded to sulphate groups.

(c) Water molecules may occupy voids (interstitial sites) in the crystal lattice, e.g.  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$

#### 12.3.4. Hard and Soft Water—Water Softening

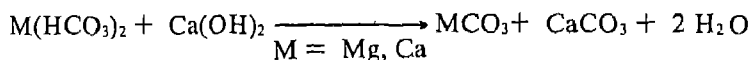
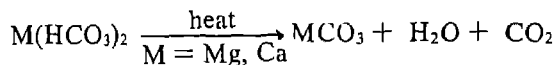
Natural water contains dissolved salts. If some of these salts (e.g.,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$ ) are present at an appreciable level, water does not form lather with soaps easily. The effectiveness of water for washing purposes is thereby reduced. We call this type of water HARD WATER. Soaps are sodium salts of fatty acids  $\text{RCOO}^-$  where R is usually a higher alkyl chain. Calcium or magnesium ions present in hard water form insoluble salts with soap and prevent the formation of lather



M = Mg or Ca

A large amount of soap will be used up in precipitating calcium or magnesium salts and only after they are completely removed, will lather be formed. Hard water poses problems when used in industrial boilers for producing steam, because it causes the formation of scales or deposits on the walls of the boilers. Removal of dissolved calcium and magnesium ions from hard water is called WATER SOFTENING.

There are two types of hardness—TEMPORARY and PERMANENT. Temporary hardness is caused by the presence of bicarbonates and this type of hardness can be removed by merely boiling the water. Boiling decomposes the bicarbonates to give carbon dioxide and insoluble carbonates which can be removed by filtration or decantation. Temporary hardness can also be removed by the addition of a calculated amount of lime whereupon magnesium and/or calcium carbonate is precipitated.

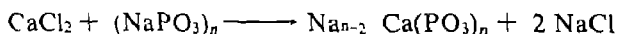


**Permanent Hardness** Permanent hardness is caused by the presence of soluble calcium or magnesium salts other than bicarbonates. These cannot be removed upon boiling. This type of hard water can be converted into soft water by one of the following methods.

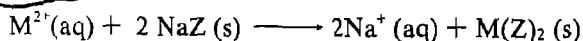
(a) By chemical additives. In this method, calcium and magnesium ions are precipitated by the addition of calculated amounts of washing soda ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ).



The bivalent ions can be rendered ineffective by the addition of sodium poly-metaphosphate. The calcium or magnesium polyphosphate formed remains in solution, but does not react with soap readily as the ions are tied up in a stable complex



(b) *Ion-Exchange Method*: Calcium and magnesium ions in hard water may be replaced by sodium ions in what is known as the *ion-exchange* process. Naturally occurring zeolites or similar synthetic complex sodium aluminium silicates are used for this purpose. When hard water is passed through such a zeolite, the bivalent cations ( $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ ) in the water sample are exchanged by equivalent amounts of sodium ions in the zeolite.



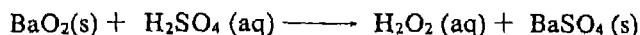
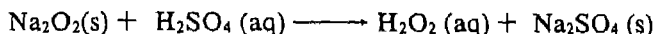
$\text{Z} = \text{anion of zeolite}$

Another class of materials which are widely used for water softening comprises organic ion-exchange resins. These resins contain a hydrocarbon chain of high molecular weight and carry covalently bound negatively charged groups such as  $-\text{SO}_3^-$  or positively charged groups of the type  $\text{NR}_3^+$ . The former type of resin will have mobile cations and the latter mobile anions. These ions can be readily exchanged for other cations or anions. By successively passing water through a cation-exchange resin (containing  $\text{H}^+$  as the positive ion) and an anion exchange resin (containing  $\text{OH}^-$  as the negative ion), virtually all the ions from water can be removed. In this way, DEIONISED WATER is obtained. The used cation- and anion-exchange resins are regenerated by washing them with a concentrated solution of an acid or a base.

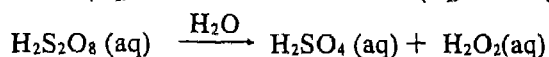
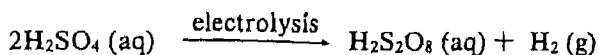
In recent years, desalination of sea water or brackish water is becoming increasingly important and several methods have been developed to obtain pure water from sea water and for recycling industrial waste water

### 12.3.5 Hydrogen Peroxide

*Preparation*: Hydrogen peroxide can be prepared in the laboratory by the action of cold, dilute sulphuric acid on sodium or barium peroxide.

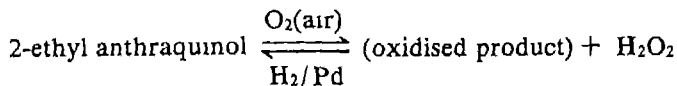


It can also be prepared by the hydrolysis of peroxydisulphuric acid, which is obtained by the electrolytic oxidation of sulphuric acid.



*H<sub>2</sub>S<sub>2</sub>O<sub>8</sub>  
electrolysis*

Industrially, the method of production of  $\text{H}_2\text{O}_2$  is by the auto-oxidation of an organic compound, 2-ethyl anthraquinol. This involves an ingenious cycle of reaction shown below. The net reaction is a catalytic union of  $\text{H}_2$  and  $\text{O}_2$  to yield hydrogen peroxide.



The hydrogen peroxide formed in the above reaction is extracted with water and the aqueous solution is concentrated by distillation (under reduced pressure) to obtain 30% (by weight) of  $\text{H}_2\text{O}_2$  solution. Further careful distillation under low pressure followed by freezing out of the remaining water produces pure  $\text{H}_2\text{O}_2$ . Hydrogen peroxide easily decomposes into water and oxygen and this process is catalysed by trace metal impurities, strong bases and exposure to light. Because of this property of  $\text{H}_2\text{O}_2$ , concentrated solutions can be dangerous as uncontrolled, rapid decomposition can result in an explosion. It is stored in coloured wax-lined bottles in the presence of a stabiliser.

#### Physical Properties and Structure:

Hydrogen peroxide is a pale blue liquid with a melting point of 272.4 K; it is somewhat more dense and viscous than water. Since  $\text{H}_2\text{O}_2$  decomposes vigorously on heating, it is not possible to determine its boiling point at atmospheric pressure; the estimated normal boiling point is 423.2 K. It is completely miscible with water.

Hydrogen peroxide molecule adopts a non-planar structure and the molecular dimensions found in the gas phase are shown in Figure 12.6. In the crystal, the dihedral angle ( $111.5^\circ$ ) reduces to  $90.2^\circ$  on account of hydrogen bonding. The two oxygen atoms are joined by a single electron-pair bond.

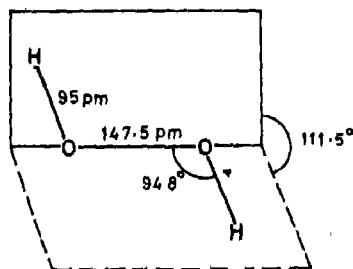
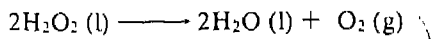


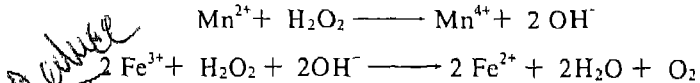
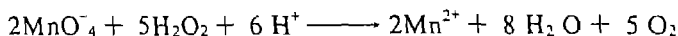
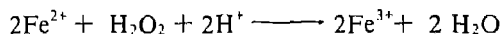
Fig. 12.6 Structure of hydrogen peroxide in the gas phase

The two oxygen atoms are joined by a single electron-pair bond.

**Reactions of Hydrogen Peroxide:** As noted above, hydrogen peroxide is unstable and decomposes to give water and dioxygen. This reaction is slow in the absence of catalysts. Decomposition is catalysed by certain metal ions (e.g.,  $\text{Fe}^{2+}$ ), metal powders (Pt, Au) and metal oxides (e.g.  $\text{MnO}_2$ ).



Hydrogen peroxide has an interesting chemistry because of its ability to function as an oxidant as well as a reductant in both acid and alkaline solutions. The oxidation state of oxygen in hydrogen peroxide is -1. It can therefore be oxidised to  $\text{O}_2$  (zero oxidation state) or reduced to  $\text{H}_2\text{O}$  or  $\text{OH}^-$  (-2 oxidation state for oxygen). On the whole, hydrogen peroxide is a very powerful oxidising agent and a poor reducing agent. Some typical oxidation and reduction reactions of hydrogen peroxide are shown below.



The oxidising property of hydrogen peroxide is put to use in the restoration of old paintings where the original white lead paint has been converted to black  $\text{PbS}$  by the  $\text{H}_2\text{S}$  in the atmosphere. Hydrogen peroxide oxidises the black  $\text{PbS}$  into white  $\text{PbSO}_4$ .



Uses The main industrial use of hydrogen peroxide is as a bleaching agent for textiles, wood and paper pulp. It is also used in the manufacture of many inorganic and organic chemicals (e.g., sodium perborate, epoxides). A dilute solution of hydrogen peroxide is used as a disinfectant for cuts and wounds. Highly concentrated  $\text{H}_2\text{O}_2$  is used as an oxidant for rocket fuel.

## 12.4 NITROGEN

Nitrogen is the first element of group 15 of the periodic table and has the electronic configuration,  $1s^2 2s^2 2p^3$ . It has five electrons in its outermost shell. Nevertheless, the maximum number of covalent bonds formed by nitrogen is limited to four (e.g.,  $\text{NH}_4^+$  salts) because it has no d orbitals in its valence level. Like oxygen and hydrogen, nitrogen exists in its elemental form as a diatomic molecule ( $\text{N}_2$ ). It is a typical non-metal with a high electro-negativity next only to that of fluorine and oxygen. Nitrogen forms a variety of compounds in all oxidation states ranging from -3 to +5. The common oxidation states are -3 (e.g.,  $\text{NH}_3$  or  $\text{Mg}_3\text{N}_2$ ), +3 (e.g.,  $\text{NaNO}_2$ ) and +5 (e.g.,  $\text{N}_2\text{O}_5$ ,  $\text{HNO}_3$ ).

Nitrogen is important for life processes as it is a constituent of plant and animal proteins. Assimilation of atmospheric nitrogen ( $\text{N}_2$ ) by plants occurs through two important NITROGEN FIXATION processes:

- During thunder storms nitrogen and oxygen of the air unite to form nitrogen oxides which are eventually converted into nitric acid and nitrates in the soil.
- Soil bacteria in the root nodules of some plants such as beans *fix* atmospheric

nitrogen into compounds that the plant can readily utilise. Many aspects of biological nitrogen fixation are still a mystery.

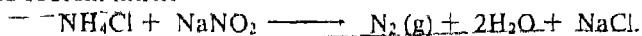
The manufacture of ammonia by the Haber process represents the principal source of industrial nitrogen fixation. Much of the ammonia manufactured is used to make fertilisers.

Molecular nitrogen comprises 78% by volume of the atmosphere. It occurs to a small extent in the earth's crust mainly as sodium nitrate,  $\text{NaNO}_3$  (called Chile salt-peter) and potassium nitrate (called salt-peter). Its total abundance in earth including the atmosphere is 0.01% by weight.

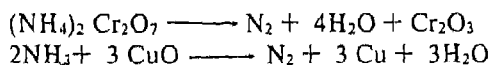
#### 12.4.1 Preparation of Dinitrogen

Dinitrogen is produced commercially from air by liquefaction and fractional distillation. Liquid nitrogen (b.p. 78 K) distills out first leaving behind liquid oxygen (b.p. 90 K). Dinitrogen derived from air contains small amounts of oxygen and some of the noble gases. Worldwide production of dinitrogen from this source is more than 50 million tonnes per annum.

In the laboratory, dinitrogen is prepared by an aqueous solution of ammonium chloride and sodium nitrite



Small amounts of  $\text{NO}$  and  $\text{HNO}_3$  are also formed in this reaction, these impurities can be removed by passing the gas through aqueous sulphuric acid containing dichromate. Other possible routes for dinitrogen are the thermal decomposition of ammonium dichromate and the reaction of ammonia with  $\text{CuO}$  at elevated temperatures:



#### 12.4.2 Properties and Reactions of Dinitrogen

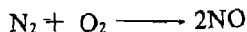
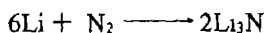
Dinitrogen is a colourless, odourless, tasteless gas. It is non-toxic. Dinitrogen has a very low solubility in water (23.2  $\text{cm}^3$  per one litre of water at  $0^\circ\text{C}$  and 1 atm pressure). Its melting and boiling points are 63.2 K and 77.2 K respectively.

Dinitrogen is chemically unreactive at ordinary temperatures. It is neither combustible nor a supporter of combustion. The  $\text{N}-\text{N}$  bond in the  $\text{N}_2$  molecule has a formal triple bond character (Unit 6) with a bond distance of 109.8 pm and is very stable (bond dissociation energy is 946  $\text{kJ mol}^{-1}$ ).

109.8 pm



At high temperatures, dinitrogen combines with many metals and non-metals to form ionic and covalent nitrides. A few typical reactions are:

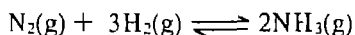


### 12.4.3 Uses of Dinitrogen

The main use of dinitrogen is in the manufacture of ammonia and other industrial nitrogen chemicals (e.g., calcium cyanamide). It also finds use where the presence of an inert gas is required (iron and steel industry, inert diluant for reactive chemicals). Liquid nitrogen is used as a refrigerant to preserve biological materials, in freezing food articles and in cryosurgery

### 12.4.4 Compounds of Nitrogen

**Ammonia** Ammonia is manufactured by the Haber process represented by the equilibrium



In accordance with Le Chatelier's principle, high pressure would favour the formation of ammonia. The optimum conditions for the production of the ammonia are, a pressure of  $200 \times 10^5$  Pa (about 200 atm), a temperature of 673 K and the use of a catalyst such as iron oxide with small amounts of K<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub> to increase the rate of attainment of equilibrium. The flow chart for the production of ammonia is shown in Fig 12.7. Annual world production of ammonia now exceeds 100 million tonnes. In India we have several large ammonia manufacturing units.

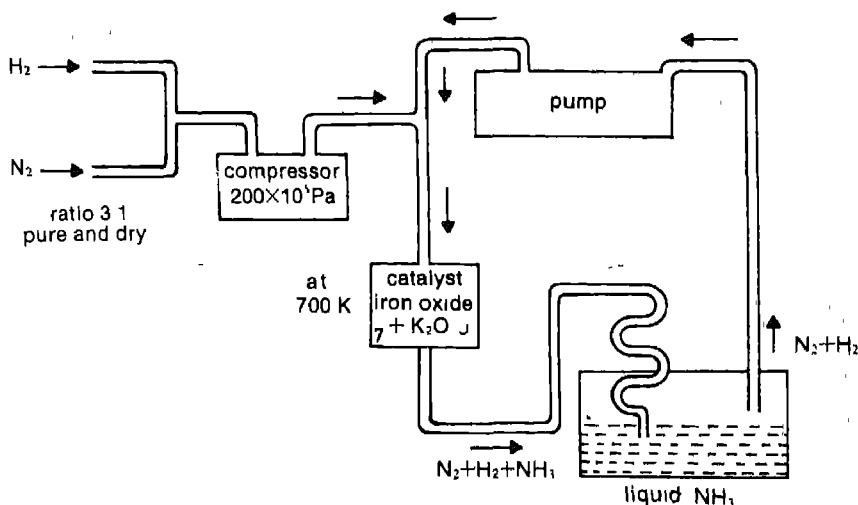
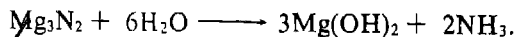
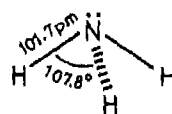


Fig 12.7 Flow chart for the manufacture of ammonia

A convenient laboratory preparation of ammonia consists of heating an ammonium salt with a strong alkali (e.g., NaOH) either in the solid form or dissolved in water. It can also be prepared by the hydrolysis of magnesium nitride.

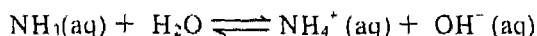


Ammonia is a colourless gas with a pungent odour. Its melting point and boiling point are 198.4 K and 239.7 K respectively. The ammonia molecule is trigonal pyramidal with the nitrogen atom at the apex.

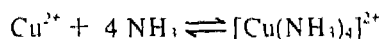


In the solid and liquid states, it is associated through hydrogen bonds as in the case of water.

Ammonia gas is highly soluble in water. Its aqueous solution is weakly basic due to the equilibrium:



The presence of a lone pair of electrons on the nitrogen atom of the ammonia molecule makes it a Lewis base. It forms coordinate linkage with metal ions and these ammonia compounds find use in qualitative analysis as shown below.



Ammonia is used mostly to produce various types of fertilisers (ammonium nitrate, urea, ammonium phosphate and ammonium sulphate) and in the manufacture of some inorganic nitrogen compounds, the most important one being nitric acid. Liquid ammonia is also used as a refrigerant.

Oxides of Nitrogen: Oxides of nitrogen provide a fascinating picture from the point of view of their varied structures and diverse chemical behaviour. They range from  $\text{N}_2\text{O}$  (oxidation state of nitrogen +1) through  $\text{NO}$ ,  $\text{N}_2\text{O}_3$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_4$  to  $\text{N}_2\text{O}_5$  in which the oxidation state of nitrogen is +5. The structures of these six oxides of nitrogen are shown below (Figure 12.8). Nitric oxide is the most important in the manufacture of nitric acid and nitrate fertilisers. In recent years  $\text{N}_2\text{O}_4$  has been used as an oxidiser for rocket fuels in missiles and space vehicles.

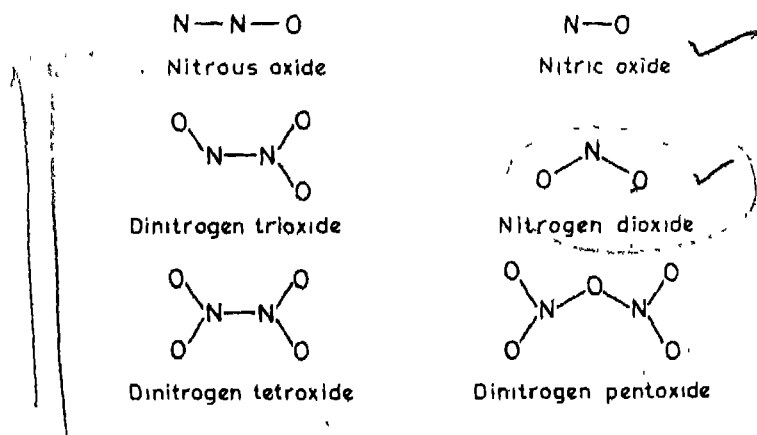
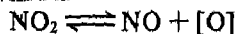


Fig 12.8 Structures of six oxides of nitrogen; only the molecular shapes are shown and bond descriptions omitted.

### SMOG

Inhabitants of metropolitan cities like Delhi, Calcutta, etc have become used to a smoky atmosphere. In the winter months, the morning fog couples with smoke and sulphur dioxide (produced by the incomplete combustion of coal) to yield what is known as SMOG.

Another kind of smog brewing up nowadays is the photochemical smog, the product of a sunny climate and smoke. Nitrogen and oxygen of the air combine with each other in the high temperature pockets (e.g., around automobile engines or furnaces) to produce colourless nitric oxide gas. Nitric oxide is further oxidised to give brown nitrogen dioxide gas that is visible as a brown layer in the atmosphere if abundantly present. Nitrogen dioxide gas dissolves in falling rain water to make it acidic. This now becomes harmful and may react further to produce a number of dangerous compounds. Nitrogen dioxide may even be decomposed by the ultraviolet rays of the sun to release nascent oxygen.

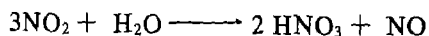
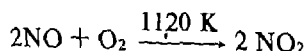
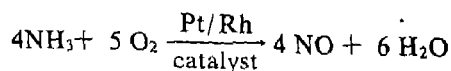


Nascent oxygen combines with molecular oxygen to give corrosive ozone that is irritating to the eyes and lungs. Many harmful compounds are also produced by incomplete oxidation of the hydrocarbon fuels.

Efforts are being made to reduce this problem by adding catalysts to the fuel that help in removing the unwanted hydrocarbons left due to incomplete oxidation of fuels and prevent the breakdown of nitric oxide to nitrogen and oxygen. However, an efficient method is yet to be discovered.

Oxides of nitrogen,  $(\text{NO})_x$  are emitted into the atmosphere during the burning of oil and coal (in power stations, refineries and automobiles) causing air pollution.

Nitric acid. Nitric acid is the most important of the oxyacids of nitrogen. It is a widely used industrial chemical and is manufactured by the catalytic oxidation of ammonia in what is known as OSTWALD PROCESS.





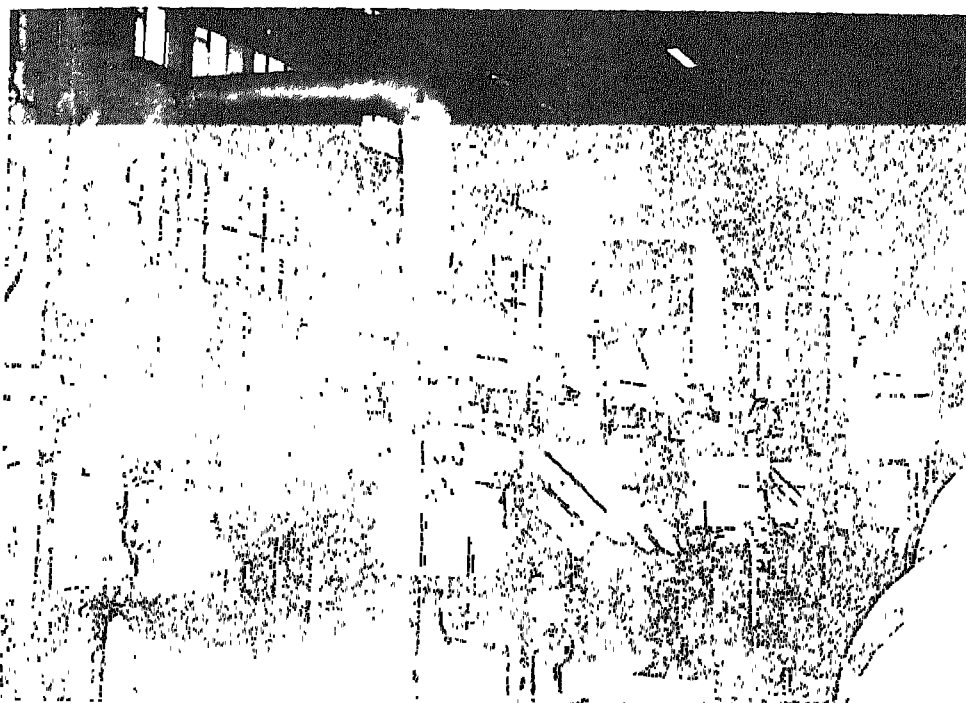
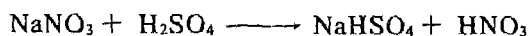


Photo I Inside view of the nitric acid plant (Nangal fertilizer factory)

Courtesy PIB, New Delhi

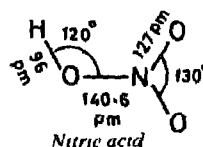
The aqueous nitric acid obtained by this method can be concentrated by distillation to ~ 68.5% by weight. Further concentration to 98% acid can be achieved by dehydration with concentrated sulphuric acid.

✓ In the laboratory, nitric acid can be prepared by heating  $\text{NaNO}_3$  or  $\text{KNO}_3$  with concentrated sulphuric acid in a glass retort



✓ Anhydrous nitric acid can be obtained by distillation of concentrated aqueous nitric acid with  $\text{P}_2\text{O}_5$ . It is a colourless liquid with melting and boiling points of 231.4 K and 355.6 K respectively. Its density at 298 K is  $1.504 \text{ g cm}^{-3}$ . Laboratory grade nitric acid contains 68% of the acid and has a specific gravity of 1.414.

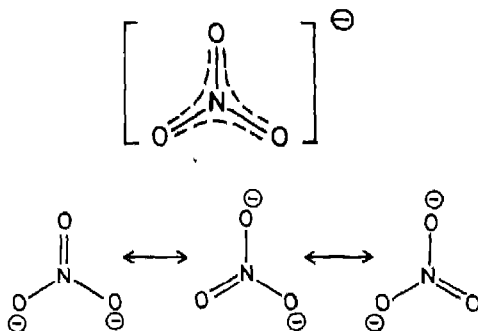
In the gaseous state,  $\text{HNO}_3$  exists as planar molecules with the structure given alongside: --



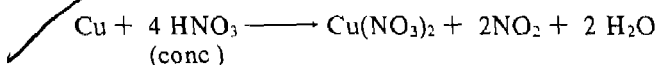
In aqueous solution, nitric acid is a strong acid and dissociates to give hydronium and nitrate ions. Neutralisation of the acid with the appropriate alkalis yields nitrates, the salts of nitric acid.



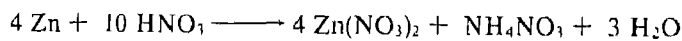
The nitrate ion,  $\text{NO}_3^-$ , is isoelectronic with carbonate ion,  $\text{CO}_3^{2-}$ , and is also planar. The nitrate ion can be represented by the resonance structures shown below.



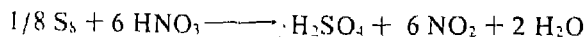
Concentrated nitric acid is a strong oxidising agent and attacks most metals except noble metals such as gold and platinum. Some metals (e.g., Cu, Al) do not dissolve in concentrated nitric acid because of the formation of a passive film on the surface. The products of reduction depend upon the concentration of the acid, temperature and the nature of the material undergoing oxidation. The principle product is nitric oxide (NO), when dilute nitric acid is used and N(IV) oxides, when conc  $\text{HNO}_3$  is used.



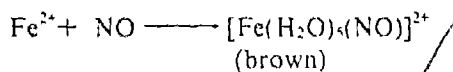
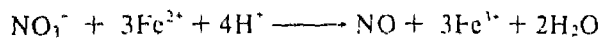
Zinc, which is a more powerful reducing agent than copper, reacts with dilute nitric acid to give ammonium nitrate.



Nitric acid also oxidises non-metals and their compounds. Iodine is oxidised to iodic acid, carbon to carbon dioxide, sulphur to  $\text{H}_2\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  and phosphorus to phosphoric acid. Nitric acid is reduced to nitrogen dioxide ( $\text{NO}_2$ ).



The familiar brown-ring test for nitrates depends on the ability of  $\text{Fe}^{2+}$  to reduce nitrates to nitric oxide which reacts with  $\text{Fe}^{2+}$  to form a brown coloured complex. The test is usually carried out by adding dilute ferrous sulphate to an aqueous solution suspected of containing nitrate ion, and then carefully adding concentrated sulphuric acid through the sides of the test tube so that a separate layer is formed. A brown ring at the interface between the solution and sulphuric acid indicates the presence of nitrate ion in solution.



*Uses of Nitric Acid:* The major use of nitric acid is in the manufacture of ammonium nitrate for fertilisers and other nitrates for use in explosives and pyrotechnics. It is also used for the preparation of nitroglycerin, trinitrotoluene, and other organic nitro compounds. Another major use is in the PICKLING OF STAINLESS STEEL and etching of metals and as an oxidiser in rocket fuels.

### EXERCISES

- 12.1 Discuss the position of hydrogen in the periodic table
- 12.2 Distinguish clearly between salt-like and covalent hydrides.
- 12.3 Describe the industrial uses of hydrogen which depend on:
  - (i) the heat liberated when it burns
  - (ii) its ability to react with vegetable oil in the presence of a catalyst
  - (iii) its ability to unite with nitrogen.
- 12.4 Why does elemental hydrogen react with other substances only slowly at room temperature?
- 12.5
  - (i) How would you prepare dihydrogen from water by using a reducing agent?
  - (ii) How would you prepare dihydrogen from a substance other than water?
  - (iii) How would you prepare very pure dihydrogen in the laboratory?
  - (iv) How would you prepare heavy hydrogen in the laboratory?
- 12.6 What are the products of the following reactions? Write balanced equations
  - (i)  $\text{Fe (s)} + \text{H}_2\text{(g)} \longrightarrow$
  - (ii)  $\text{PbS(s)} + \text{H}_2\text{O}_2\text{(g)} \longrightarrow \text{PbSO}_4 + \text{H}_2\text{O}$
  - (iii)  $\text{MnO}_4^-\text{(aq)} + \text{H}_2\text{O}_2\text{(aq)} \longrightarrow 2\text{Mn}^{2+} + 3\text{H}_2\text{O} + 5\text{O}_2$
  - (iv)  $\text{O}_2\text{(g)} + \text{S}_8\text{(s)} \longrightarrow$
- 12.7 State whether each of the following compounds is a basic or an acidic anhydride. Write a balanced equation for the reaction with water in each case.  
 $\text{Na}_2\text{O}$ ,  $\text{P}_4\text{O}_{10}$ ,  $\text{SO}_2$ ,  $\text{Al}_2\text{O}_3$ .

- 12.8 What is the shape of the ozone molecule?
- 12.9 Write Lewis dot structure(s) for ozone molecule and explain why the O-O distances in ozone are equal.
- 12.10 What is the importance of ozone for plant and animal life on earth?
- 12.11 What is the importance of heavy water with regard to nuclear power generation?
- 12.12 How is heavy water produced from ordinary water?
- 12.13 Why does water have a high boiling and a high melting point compared to  $\text{H}_2\text{S}$ ?
- 12.14 Describe the structure of the common form of ice.
- 12.15 Distinguish clearly between (i) hard and soft water, (ii) temporary hardness and permanent hardness
- 12.16 What are the different methods used for the softening of hard water? Explain the principle of each method.
- 12.17 What are the ways in which water molecules are bonded to an anhydrous salt to form a hydrate?
- 12.18 Why is water an excellent solvent for ionic or polar substances?
- 12.19 Why does hard water not form lather with soap?
- 12.20 How is hydrogen peroxide manufactured?
- 12.21 What is the structure of hydrogen peroxide? Draw a schematic diagram indicating the shape of the molecule clearly
- 12.22 Explain why  $\text{H}_2\text{O}_2$  cannot be stored for prolonged periods.
- 12.23 Show how hydrogen peroxide can function both as a reducing and as an oxidising agent.
- 12.24 Hydrogen peroxide is used to restore the colour of old oil-paintings containing lead oxide. Write a balanced equation for the reaction that takes place in this process
- 12.25 Give examples of compounds in which nitrogen exhibits oxidation states of  $-3$ ,  $+3$  and  $+5$ .
- 12.26 Give an equation for the reaction that takes place on heating ammonium dichromate.
- 12.27 Discuss the principles involved in the Haber's process for the manufacture of ammonia
- 12.28 Explain the following observations.  
(i)  $\text{NH}_3$  has a higher boiling point than  $\text{PH}_3$   
(ii) Ammonia is a good complexing agent  
(iii) Nitrogen does not form any pentachloride.
- 12.29 Describe two distinct routes for the conversion of atmospheric dinitrogen to compounds which ultimately lead to the formation of amino acids and proteins in our body
- 12.30 Write balanced equation(s) for the manufacture of nitric acid by the oxidation of ammonia
- 12.31 What is the structure of nitric acid?
- 12.32 Illustrate how a metal can give different products with nitric acid. Give balanced equations.

- 12.33 Describe the uses of nitric acid
- 12.34 How is dinitrogen prepared in the laboratory?
- 12.35 Identify the products of the following reactions (Give balanced equations).
- (i)  $\text{Mg}_2\text{N}_3 + \text{H}_2\text{O} \longrightarrow$
  - (ii)  $\text{I} + \text{HNO}_3 \longrightarrow$
  - (iii)  $\text{Cu} + \text{HNO}_3 \text{ (Concentrated)} \longrightarrow$
  - (iv)  $\text{Li} + \text{N}_2 \longrightarrow$
- 12.36 Illustrate how nitrogen compounds provide good examples of *multiple bonding* and *resonance*
- 12.37 What is the mass of hydrogen peroxide present in 1 litre of a 2 M solution? Calculate the volume of oxygen at STP liberated upon the complete decomposition of 100 cm<sup>3</sup> of the above solution.
- 12.38 How would you prepare a sample of  $\text{ND}_3$ ?

## UNIT 13

### CHEMISTRY OF NON-METALS-II

(Boron, Silicon, Phosphorus, Sulphur, Halogens and the Noble Gases)

*Silicon is everywhere in Nature, in rocks, clays and sand; it's only next to oxygen in abundance. Without elemental silicon there would have been no modern electronic revolution.*

1																18
	2															He
																Ne
																Ar
																Kr
																Xe
																Rn

#### OBJECTIVES

In this Unit, we shall learn

- \* the chemistry of boron, boric acid and borates;
- \* the chemistry of silicon, phosphorus and sulphur;
- \* the preparation and properties of phosphoric acid, phosphatic fertilisers and sulphuric acid,
- \* the occurrence, preparation and properties of halogens;
- \* the chemistry of noble gases

IN THE PREVIOUS UNIT we learnt about the chemistry of three typical non-metals—hydrogen, oxygen and nitrogen—belonging to the first and second periods of the periodic table. In this Unit, we shall take up for study the chemistry of a few more non-metals—boron, silicon, phosphorus, sulphur, halogens and the noble gases. Although boron belongs to Group 13 of the periodic table, it shows similarities to both its neighbours, carbon and silicon. Carbon comes next to boron in the periodic table and silicon is located diagonally across. Silicon, phosphorus and sulphur, being elements of the third period of the periodic table, have larger sizes and lower first members of their respective groups (carbon, nitrogen) characteristics lead to substantial differences in the chemistry of Si, P and S compared with their group partners, C, N and O respectively.

Halogens, as a class, show much more similarities in their chemical behaviour than any other group of elements except groups 1 and 2. The discovery of noble gases and their very high chemical stability have played an important role in the development of the periodic table and the theories of chemical bond. Although they had been regarded as totally inert for a long time, in the last two decades, several compounds of noble gases (particularly of xenon) have been prepared. We shall discuss these aspects very briefly. We shall also study the manufacture and uses of some important industrial chemicals such as sulphuric acid, phosphoric acid, phosphatic fertilisers and hydrochloric acid.

### 13.1 BORON

Boron is the first member of group 13 of the periodic table and is the only non-metal of this group. Its electronic configuration is  $1s^2 2s^2 2p^1$  with three electrons in the valence shell. The chemistry of boron is in several respects different from that of the other members of Group 13. Because of its small size, high ionisation energy and low electronegativity, boron forms a variety of covalent molecular compounds. In this respect, boron resembles carbon and silicon. However, since the number of valence electrons (three) in boron is one less than the number of valence orbitals (four), boron compounds, especially the hydrides, are usually referred to as ELECTRON DEFICIENT compounds. Because of their electron deficient nature, boron compounds can readily accept electrons from molecules which can donate electrons. Boron compounds thus behave as Lewis acids.

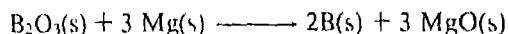
#### 13.1.1 Occurrence

The abundance of boron in the crust of the earth is low ( $\sim 0.001\%$ ). Boron occurs mainly as borates and orthoboric acid. The important minerals of boron are BORAX  $\text{Na}_2[\text{B}_4\text{O}_7(\text{OH})_4] \cdot 8\text{H}_2\text{O}$ , KERNITE  $\text{Na}_2[\text{B}_4\text{O}_7(\text{OH})_4]$  and COLEMANITE  $\text{Ca}_2[\text{B}_6\text{O}_{11}(\text{OH})_2] \cdot 2\text{H}_2\text{O}$ . Commercially viable deposits of borates are found in California (U.S.A.) and Turkey. In India, borax occurs in Puga Valley, Ladakh and Sambhar Lake, Rajasthan.

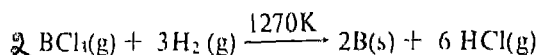
### 13.1.2 Isolation

Elemental boron is obtained by one of the following four methods.

- (a) reduction of oxides by electropositive metals;



- (b) the reduction of a volatile boron compound by dihydrogen at high temperatures,



- (c) electrolytic reduction of fused borates or other boron compounds (e.g.,  $\text{KBF}_4$ ) at 1000 K or above, and  
(d) thermal decomposition of boron hydrides.

### 13.1.3. Physical Properties

Boron is an extremely hard solid with a melting point greater than 2450 K. At least three allotropic forms of boron are known. It has a low electrical conductivity. It occurs in two isotopic forms,  $^{10}\text{B}$  (~20%) and  $^{11}\text{B}$  (~80%).

### 13.1.4 Chemical Properties and Reactions

Boron is unreactive to most chemical reagents at ordinary temperature except towards strong oxidising agents such as fluorine and concentrated nitric acid. It combines with metals at very high temperatures to form borides which are generally hard, high-melting solids.

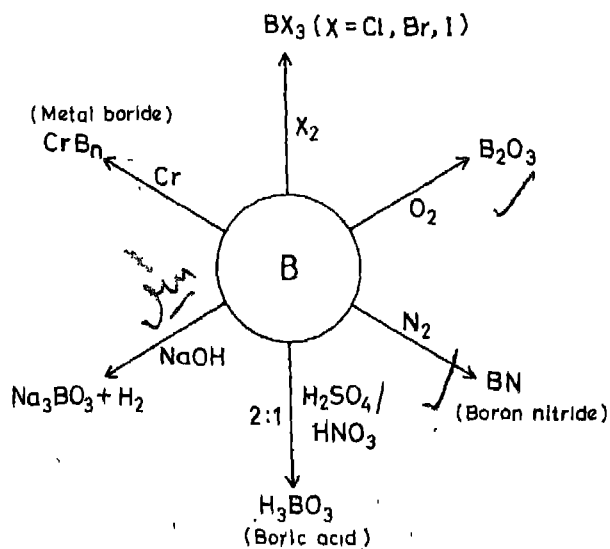


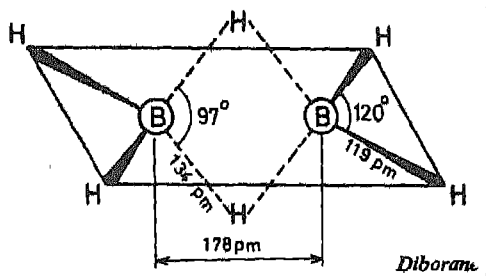
Fig 13.1 Some reactions of elemental boron



Boron combines with oxygen, nitrogen and halogens at elevated temperatures to yield boron trioxide, boron nitride and boron trihalides respectively. It reacts with fused caustic alkalis forming borates with the evolution of hydrogen (Fig 13.1)

In view of the trivalency of boron, we would expect it to form a simple hydride,  $\text{BH}_3$ . However, this is not the case. The simplest boron hydride is diborane,  $\text{B}_2\text{H}_6$ . Besides diborane, boron forms a number of higher hydrides (e.g.,  $\text{B}_5\text{H}_9$  and  $\text{B}_4\text{H}_{10}$ ).

The structure of diborane is shown alongside:



The four terminal hydrogen atoms and the two boron atoms lie in one plane. Above and below this plane, there are two bridging hydrogen atoms. Each boron atom forms four bonds even though it has only three electrons. The terminal B-H bonds are regular bonds but the bridge B-H bonds are different.

### 13.1.5 Borax and Boric Acid

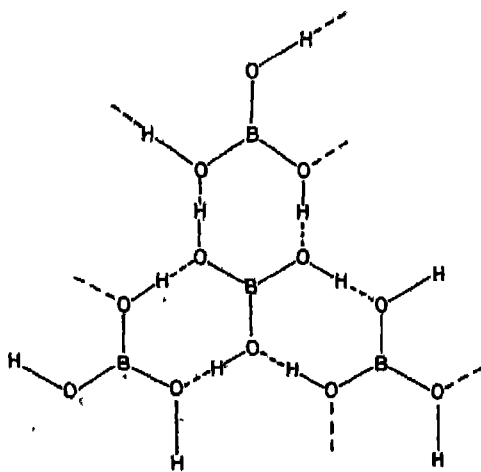
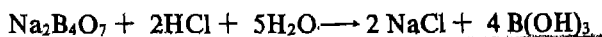


Fig. 13.2 Structure of boric acid; the dotted lines represent hydrogen bonds

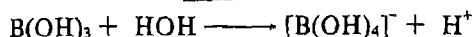
Boron forms strong bonds with oxygen as reflected in the invariable occurrence of borates in nature (section 13.1.1). The basic structural unit in borates can have one or more boron atoms linked together by intervening oxygen atoms in the form of chains and or rings. Borax contains the tetranuclear units  $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ ; its correct formula is therefore  $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$ . Borax dissolves in water to give alkaline solutions. Borax is therefore used as a water softener and cleaning agent.

Boric acid is the trivial name for orthoboric acid,  $\text{H}_3\text{BO}_3$ . It is usually prepared by acidifying an aqueous solution of borax:



Boric acid is also formed by the hydrolysis (reaction with water or dilute acid) of most boron compounds (halides, hydrides, etc.). It is a white crystalline substance. It has a layer structure in which planar  $\text{BO}_3$  units are joined by hydrogen bonds as shown in Fig. 13.2.

Boric acid is a weak monobasic acid. It differs from other protonic acids. It does not act as a proton donor but acts as a Lewis acid by accepting a hydroxyl ion: in



Heating orthoboric acid above 370 K leads to partial removal of water to yield metaboric acid, HBO<sub>2</sub>; further heating yields boric oxide, B<sub>2</sub>O<sub>3</sub>, which is the principle oxide of boron.



### 13.1.6 Uses of Boron and Its Compounds

The main industrial application of borax and boric acid is in the manufacture of heat resistant borosilicate glass (e.g., pyrex). Borax is also used as a flux for soldering metals and for making porcelain enamels. A solution of boric acid in water is commonly used as a mild antiseptic. Because of the very high ability of boron-10 (<sup>10</sup>B) isotope to absorb neutrons, metal borides are used in nuclear industry as protective shields and control rods. Boron filaments are used in making light, composite materials for aircraft.

## 13.2 SILICON

Silicon is the second member of group 14, appearing just below carbon in the periodic table and has the electronic configuration, 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>2</sup>. We would therefore expect similarities between silicon and carbon. This is indeed so upto a point. Thus silicon forms compounds such as SiH<sub>4</sub> and SiX<sub>4</sub> (X = halogens) (just as carbon forms CH<sub>4</sub> and CX<sub>4</sub>); silicon has a tetrahedral geometry in these compounds. There are also considerable differences between the chemistry of silicon and that of carbon. For example, carbon dioxide (CO<sub>2</sub>) is a gas whereas silicon dioxide (SiO<sub>2</sub>) is a high-melting solid. The reasons for the differences are:

- Silicon atom has a larger size (117pm) than carbon (77pm) and as a result, the Si-O bonds are considerably stronger than Si-Si or Si-H bonds.
- Silicon forms multiple bonds with itself with great reluctance and does not form a double bond with oxygen unlike carbon which forms numerous compounds containing C=C, C≡C and C=O groups (Unit 7.)
- Silicon can utilise 3d orbitals for bonding and can form penta- and hexa-coordinated compounds.

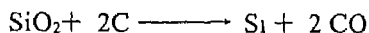
Silicon is of great importance in electronic, glass and cement industries. Much of modern electronic industry depends on devices made from elemental silicon.

### 13.2.1. Occurrence, Preparation and Properties of Silicon

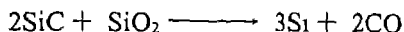
Silicon does not occur in nature as the free element but its abundance (27.2%) in the earth's crust is second only to oxygen (45.5%). It is present everywhere in the form of silica (SiO<sub>2</sub>) and silicates which contain silicon-oxygen bonds and metal

ions. Rocks and clays comprise of silicate minerals.

Elemental silicon is made by the reduction of sand (which is largely  $\text{SiO}_2$ ) with coke in an electric arc furnace.



An excess of sand is used to prevent the formation of silicon carbide.



Silicon obtained by this method is generally 96-98% pure and is mostly used in metallurgical industry to produce ferrosilicon and other alloys. It is also the starting material for the production of SILICON POLYMERS. These polymers contain a Si-O-Si framework with hydrocarbyl substituents. They are heat-resistant and water-repellant and find a variety of applications.

Very high purity silicon is required to make semiconductors for transistor applications. This grade of silicon is made by the reduction of highly purified  $\text{SiCl}_4$  or  $\text{SiHCl}_3$  with dihydrogen or by the decomposition of  $\text{SiH}_4$ .

Elemental silicon has a shining metallic lustre with a melting point of 1793 K and a boiling point of  $\sim 3550$  K. It has a diamond structure. It is particularly unreactive at room temperature towards all elements except fluorine. It combines with other halogens and elemental oxygen and nitrogen at high temperatures. It also combines directly with magnesium and other metals at the temperature of the electric furnace (2000 - 2500 K) to form compounds such as  $\text{Mg}_2\text{Si}$ .

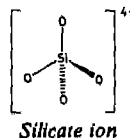
Unlike carbon, silicon dissolves in hot aqueous alkali to liberate hydrogen.



The binary compound of silicon with carbon ( $\text{SiC}$ ) is known as CARBORUNDUM which is used as an abrasive and refractory material.

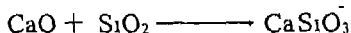
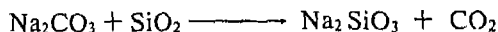
### 13.2.2. Silicates, Silica and Glass

Rocks and its weathered products (soils, clays and sands) consist of almost entirely silicate minerals and silica. Among the silicate minerals, we should specially mention quartz, mica, asbestos, feldspars and zeolites. The basic structural unit in silicates and silica is the  $(\text{SiO}_4)^{4-}$  ion which is arranged in various ways to build up chains, ribbons, rings, sheets and three dimensional networks. Silica occurs in various forms and is used extensively in industry and laboratory. Silica gel is used as desiccant and as a chromatographic support. Vitreous silica is used to make glass-ware.



Two of the important man-made silicates from a practical point of view are glass and cement. We shall learn about cement in Unit 14. Here we shall briefly deal with the different types of glasses and how we can make them.

When molten silicates are cooled rapidly, we get a transparent and non-crystalline material, called glass. Glass is not a true solid, it has no definite melting point. It softens when heated to a certain temperature. Ordinary glass is a mixture of sodium and calcium silicates and is produced by heating a mixture of sodium carbonate, calcium oxide and silicon dioxide (or sand) in a furnace around 1700 K.



This type of glass is known as SODA GLASS or SOFT GLASS which has an approximate composition,  $\text{Na}_2\text{SiO}_3$ ,  $\text{CaSiO}_3$ ,  $4\text{SiO}_2$ . Addition of transition metal compounds to the glass mix gives coloured glasses. Small amounts of Cr (III), Mn (IV),  $\text{Co}^{2+}$  (II) or Fe (III) compounds impart green, violet, blue or brown colour respectively. Lead-potash glass has a high refractive index and is used for making cut-glass objects and lenses for optical purposes. Addition of boric oxide or borax to replace part of  $\text{SiO}_2$  leads to a heat-resistant borosilicate glass with a low coefficient of thermal expansion. This type of glass (trade name *pyrex*) is used for making laboratory glassware; as it can withstand sudden changes of temperature.

### 13.3 PHOSPHORUS

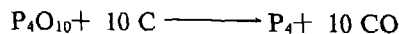
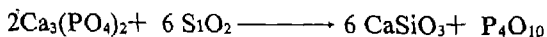
Phosphorus is the second member of group 15 of the periodic table and has the electronic configuration,  $1s^2 2s^2 2p^6 3s^2 3p^3$ . It is an analogue of nitrogen with the same number of valence electrons, but differs from nitrogen considerably in its chemical behaviour. Some of these differences can be accounted for on the basis of the larger size and the lower electronegativity of phosphorus compared with nitrogen. Whereas nitrogen forms numerous compounds in which it has  $sp$  or  $sp^2$  hybridisation, these hybridisation states are not particularly stable for phosphorus. Phosphorus compounds play an important role in life processes, several of its compounds have also industrial applications. The most important of these chemicals are orthophosphoric acid and phosphatic fertilisers.

#### 13.3.1. Occurrence

Phosphorus occurs mainly in the form of phosphate minerals in the crust of the earth. The most common minerals are hydroxyapatite,  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  and fluorapatite,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ . Vast deposits of phosphate rocks occur in North Africa and North America. In India, commercially viable phosphate rock deposits are found in Rajasthan. Phosphorus is an essential constituent of animal and plant matter. It is present in bones (as inorganic phosphate) and also in living cells (in DNA).

#### 13.3.2. Preparation and Properties

Elemental phosphorus is obtained by heating phosphate rock with coke and silica in an electric furnace at about 1770 K. The reaction may be represented as:



The phosphorus so obtained is WHITE PHOSPHORUS which exists as discrete  $P_4$  molecules. It is extremely reactive towards many reagents. It spontaneously ignites in air and shows a glow, thus deriving its name PHOSPHORUS meaning light bringing. It is soluble in solvents such as carbon disulphide. Its melting point is 317 K.

Phosphorus exhibits allotropy. In addition to white phosphorus, there are two other allotropes, RED PHOSPHORUS and BLACK PHOSPHORUS. Red phosphorus is obtained by heating white phosphorus at 540-570 K out of contact with air for several hours. It is less reactive and less soluble than white phosphorus. Red phosphorus has a polymeric structure as shown in Fig 13.3. At room temperature, the stable modification of elemental phosphorus is the red allotrope. Black phosphorus is made by heating white phosphorus to 470 K under high pressure. Black phosphorus exists in three crystalline and one amorphous form. Only at temperatures greater than 1070 K does phosphorus vapour dissociate to give  $P_2$  molecules. This behaviour may be compared with the extreme stability of dinitrogen at room temperature (Can you suggest why?)

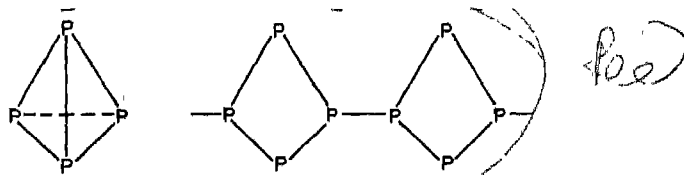
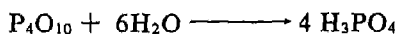
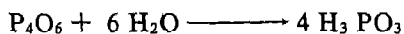


Fig. 13.3 Structures of white and red phosphorus

The three important oxidation states of phosphorus are  $-3$ ,  $+3$  and  $+5$  typified by the compounds, calcium phosphide ( $Ca_3P_2$ ), phosphorus trichloride ( $PCl_3$ ) and phosphorus pentachloride ( $PCl_5$ ).

### 13.3.3. Oxides and Oxyacids of Phosphorus

When phosphorus is burnt in a limited supply of oxygen, it forms phosphorus trioxide which is formulated as  $P_4O_6$ . With an excess of air or oxygen, the higher oxide of phosphorus called phosphorus pentoxide is formed. Phosphorus pentoxide consists of discrete  $P_4O_{10}$  molecules. It is a powerful dehydrating agent. Both phosphorus trioxide and phosphorus pentoxide are acidic oxides which dissolve in water to give phosphorous and phosphoric acid,  $H_3PO_3$  and  $H_3PO_4$ , respectively.



The latter acid is known as ORTHO PHOSPHORIC ACID and its structure is shown in (Fig. 13.4). Salts of orthophosphoric acid are known as orthophosphates. Since ortho-

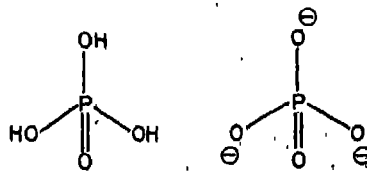
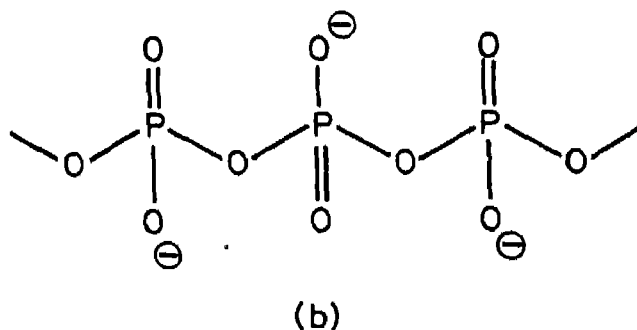
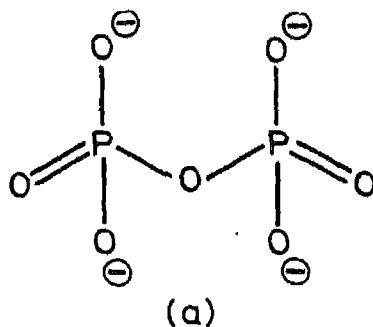


Fig. 13.4 Structures of orthophosphoric acid and phosphate ion

phosphoric acid is tribasic, three series of salts are possible; these are dihydrogen phosphates, mono hydrogen phosphates and normal phosphates. Like  $\text{SiO}_4^{4-}$  and  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  has a tetrahedral structure (Fig 13.4)

The chemistry of the acids of phosphorus is quite complicated. Two or more  $\text{PO}_4^{3-}$  units can join together to give what is known as condensed phosphates, a situation analogous to that found in silicate structures. The structure of pyrophosphate (formula  $\text{P}_2\text{O}_7^{4-}$ ) and metaphosphate ions (empirical formula  $\text{PO}_3^-$ ) are shown alongside and below respectively. Metaphosphates can be cyclic or can have linear chains



Phosphate groups play an important role in biology for energy storage. Hydrolysis of P—O—P link releases energy which can be put to useful work

Orthophosphoric acid is a major industrial chemical. It is manufactured from phosphate rocks and the acid obtained in this way is used for the production of phosphate esters. Pure acid derived from elemental phosphorus via and hydrolysis of  $\text{P}_4\text{O}_{10}$  is used for the preparation of phosphate salts which find applications in food, detergent and pharmaceutical industries.

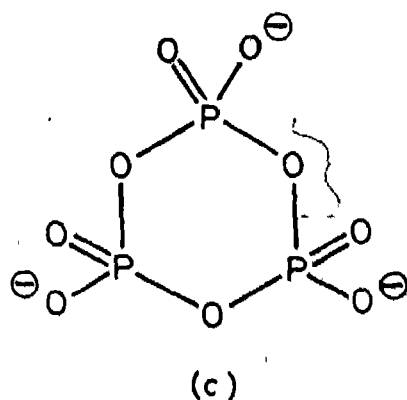


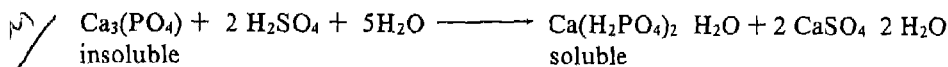
Fig. 13.5 Structures of (a) Pyrophosphate (b) Linear metaphosphate ions (c) Cyclic metaphosphate

#### 13.3.4. Chemical Fertilisers

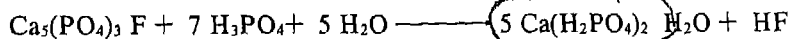
The fertility of the soil can be increased by using artificial chemical fertilisers. The chemical fertilisers can be classified into three types:

- (a) *Nitrogenous fertilisers*. The most important of which are ammonium sulphate, ammonium nitrate, calcium ammonium nitrate, calcium cyanamide and urea
- (b) *Phosphatic fertilisers*. The most important of which is superphosphate of lime,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ .
- (c) *Mixed fertilisers*. This category of fertilisers contains a mixture of an ammonium salt, ammonium phosphate, super phosphate and potassium salt. It is known as NPK mixture

Phosphatic fertilisers such as superphosphate of lime is obtained from phosphatic rocks by treatment with concentrated sulphuric acid. In this way, insoluble phosphate rock is rendered soluble in water for use as a source of this essential plant nutrient.



Treatment of phosphate rock with phosphoric acid leads to the formation of triple superphosphate,  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  which is free from calcium sulphate and hence contains a greater percentage of phosphorus



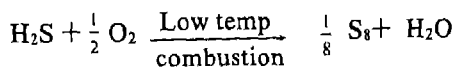
### 13.4 SULPHUR

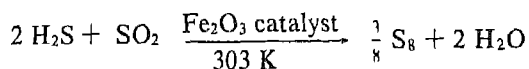
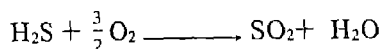
The chemistry of sulphur differs from that of oxygen in the same way as the chemistry of phosphorus differs from that of nitrogen. The electronic configuration of sulphur is  $1s^2 2s^2 2p^6 3s^2 3p^4$ . Thus sulphur can form compounds in which it has an oxidation state of  $-2$  as in the case of oxygen. Sulphur also shows oxidation states of  $+2$ ,  $+4$  and  $+6$ . It exhibits a maximum covalency of six as in  $SF_6$ . The most important industrial chemical obtained from sulphur is sulphuric acid.

#### 13.4.1. Occurrence and Extraction

Sulphur occurs in the earth's crust to the extent of 0.05%. It is mostly found in rocks as metal sulphates and sulphides. It also occurs in the elemental form in large underground beds. Another major source of sulphur is  $H_2S$  present in natural gas and crude oil.

Sulphur is extracted from underground deposits by pumping superheated water ( $\sim 440\text{ K}$ ) down the beds to melt the element and then blowing out the molten sulphur with compressed air. Recovery of sulphur from natural gas includes separating out  $\text{H}_2\text{S}$  by absorption in monoethanolamine and then converting  $\text{H}_2\text{S}$  into sulphur by the following sequence of reactions





Most of the sulphur produced is used to make sulphuric acid and other industrially important sulphur compounds. Sulphide ores when heated give off sulphur dioxide which can be directly used for the manufacture of sulphuric acid (see section 13.4.3)

### 13.4.2 Properties and Reactions

Sulphur exhibits allotropy. The two important allotropic modifications of sulphur are the rhombic and the monoclinic forms. Rhombic sulphur is stable at room temperature whilst monoclinic sulphur is stable above 369 K. Both rhombic and monoclinic sulphur consist of eight sulphur atoms combined in a ring but differ from each other in the symmetry of their crystals. The  $\text{S}_8$  ring is puckered as shown in Fig. 13.6. Several other cyclic modifications of sulphur containing 6-20 sulphur atoms per ring have been synthesised in recent years. Another form of sulphur known as plastic or amorphous sulphur is obtained by pouring liquid sulphur into water. Amorphous sulphur probably consists of long strings of sulphur atoms formed by opening of the  $\text{S}_8$  rings.

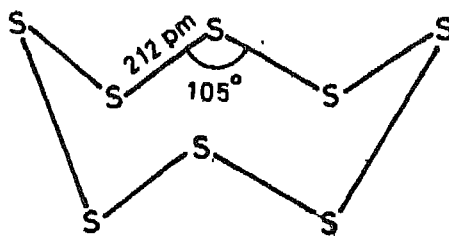
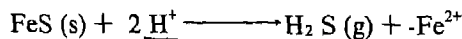


Fig 13.6 Structure of octasulphur

Elemental sulphur is reactive at slightly elevated temperatures. It combines directly with all elements except the noble gases, iodine, tellurium, nitrogen and the noble metals (e.g., gold and platinum). With metals sulphur forms sulphides which contain  $\text{M}^{n+}$  and  $\text{S}^{2-}$  ions. Treatment of sulphides with acids gives hydrogen sulphide ( $\text{H}_2\text{S}$ ) which is a foul-smelling poisonous gas. You must have seen the familiar Kipp's apparatus for the generation of  $\text{H}_2\text{S}$  in the laboratory.



What do you think would be the structure of hydrogen sulphide?  
Is this molecule linear or bent?

Metal sulphides except those of Groups 1 and 2 are almost insoluble in water.



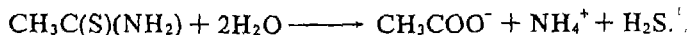
### ACID RAIN

Falling rain is usually slightly acidic due to the dissolution of atmospheric carbon dioxide in water. However, in industrial areas, oxides of sulphur and nitrogen produced by the combustion of coal and oil, may rise to the upper layers of the atmosphere and dissolve in rain water to make it as acidic as vinegar.

Acid rain can lead to extensive damage to marble monuments. It also makes the existence of marine life difficult. Aluminium compounds present in the soil are attacked and washed away to the lakes by acid rain. This causes poisoning of fish. Nitrogen fixing bacteria in the soil may also be killed and the essential macro-and micro-nutrients be washed away from the soil. In fact forest deterioration has begun in many parts of the world due to acid rain.

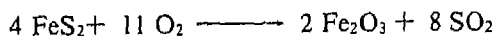
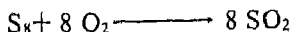
Neutralising the acid by adding lime to water is one solution to this problem. Another solution is to disperse sulphur dioxide through high smoke shafts. However, the only long-term effective method is to minimise the use of fossil fuels (coal and oil) by replacing them with smokeless sources of energy.

✓ The solubility of the sulphides can be controlled by the pH of the solution and hence  $H_2S$  finds extensive use in the qualitative analysis of metal ions. Hydrogen sulphide can be generated directly in solution by heating thioacetamide dissolved in water.

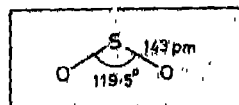


#### 13.4.3. Oxides of Sulphur and Sulphuric Acid

Sulphur forms several oxides of which sulphur dioxide ( $SO_2$ ) and sulphur trioxide ( $SO_3$ ) are the most important. Sulphur dioxide is formed by burning sulphur in air or roasting metal sulphides in the presence of air.



It is a colourless gas with an irritating odour. It is a bent molecule like  $H_2O$  as shown alongside.



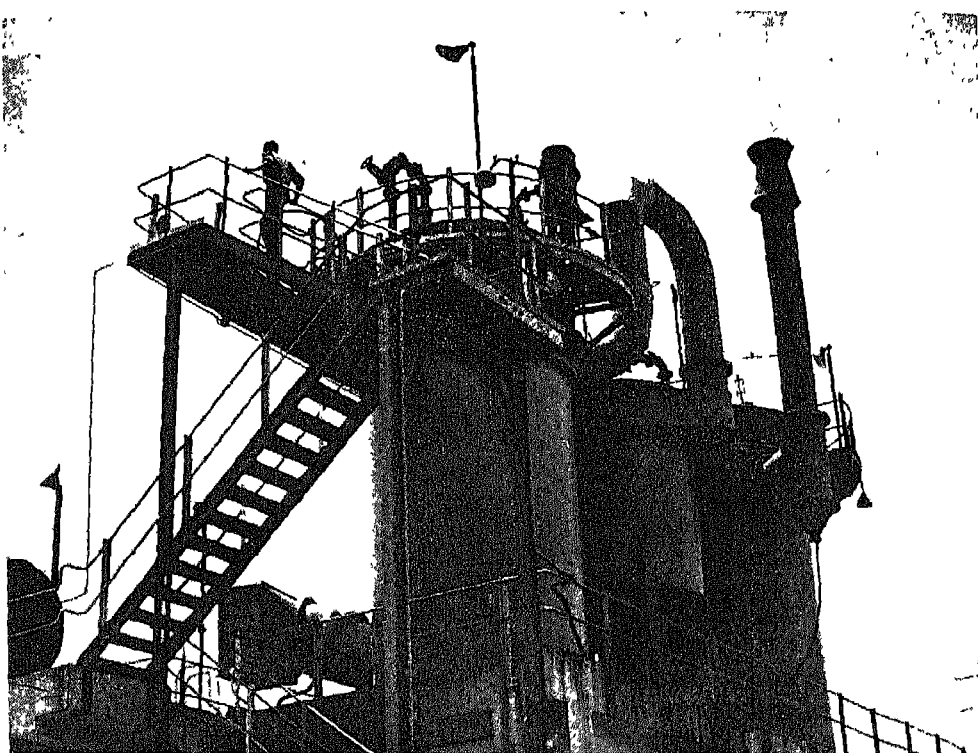


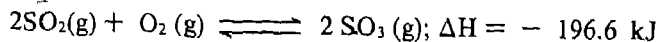
Photo II Sulphuric acid plant

Courtesy: PIB, New Delhi

Can you write the Lewis dot formula for  $\text{SO}_2$  and guess why the two S-O distances are the same?

A large amount of  $\text{SO}_2$  gas is released into the atmosphere from coal and oil-based power plants, oil-refinery operations and copper-smelting plants. The emission of  $\text{SO}_2$  causes severe environmental pollution and methods have been devised to control the levels of  $\text{SO}_2$  emissions from industrial plants.

Sulphur trioxide is formed by the direct oxidation of sulphur dioxide with atmospheric oxygen. Monomeric  $\text{SO}_3$  in the gas phase has a planar structure with a S-O distance of 142 pm. (Sulphur trioxide is anhydride of sulphuric acid.) The key step in the manufacture of sulphuric acid is the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$ , which is a slow, reversible and exothermic reaction:



To increase the rate of attaining the equilibrium, a catalyst such as divanadium pentoxide or finely divided spongy platinum is used at a pressure of 2 atmospheres and a temperature of  $\sim 700 \text{ K}$ . The manufacture of  $\text{SO}_3$  in this way is known as **CONTACT PROCESS**. Can you apply Le Chatelier's principle (Unit 9) for this reaction and predict the optimum conditions?

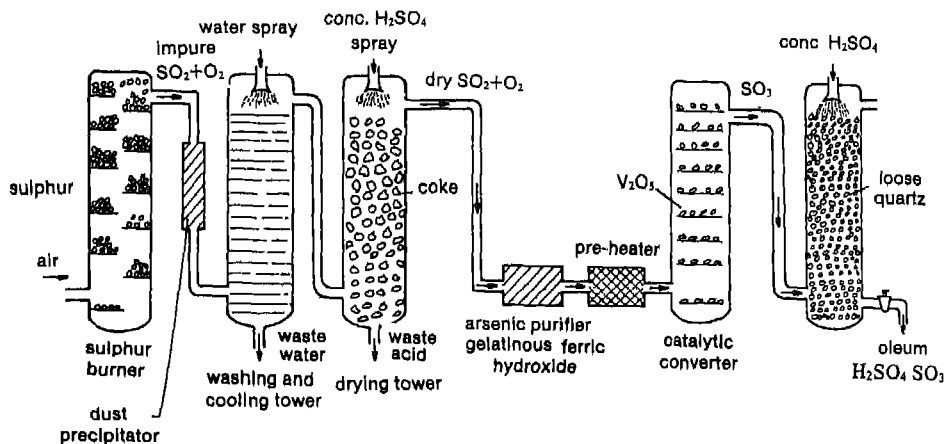
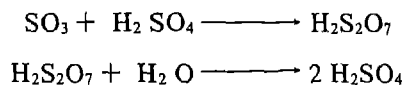


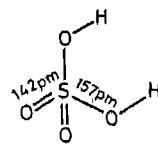
Fig 13.7 Flow diagram for the manufacture of sulphuric acid

A flow diagram for the manufacture of sulphuric acid is shown in Fig 13.7. Sulphur trioxide gas from the catalytic chamber is passed through sulphuric acid to obtain oleum. If  $\text{H}_2\text{SO}_4$  of the desired concentration is required in industry, the two steps are carried out simultaneously to make the process a continuous one and to keep the cost down.



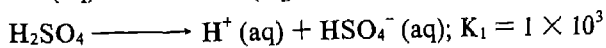
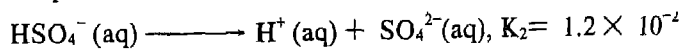
#### 13.4.4 Properties of Sulphuric Acid

Sulphuric acid is a colourless, dense, oily liquid with a specific gravity of 1.84 at 288 K. The acid freezes at 283 K and boils at 590 K. It dissolves in water with the evolution of a large quantity of heat. Hence care must be taken while preparing sulphuric acid solution from concentrated sulphuric acid which is ~ 98% and is 18 M. The concentrated acid must be added slowly into water with constant stirring. The structure of sulphuric acid in the vapour phase can be schematically represented as shown above.

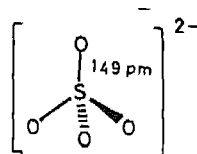


Sulphuric acid

The chemical reactions of sulphuric acid are a result of the following characteristics: (a) low volatility, (b) strong acidic character, (c) strong affinity to water, and (d) ability to act as an oxidising agent. In aqueous solution, sulphuric acid ionises in two steps:

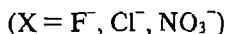
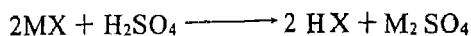


The acid forms two sets of salts—normal sulphates (such as sodium sulphate and copper sulphate) and acid sulphates (e.g., sodium bisulphate). The sulphate ion is tetrahedral as shown alongside;

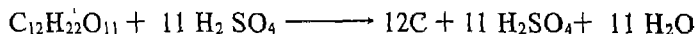


You must be familiar with the laboratory test for sulphate ion. When a soluble barium salt solution is added to a solution containing sulphate ions, a white precipitate of  $\text{BaSO}_4$  is obtained which is insoluble in dilute mineral acids.

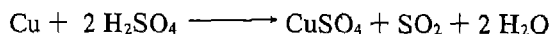
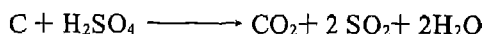
The low volatility of sulphuric acid is put to use in the manufacture of more volatile acids from their salts:



Concentrated sulphuric acid is a strong dehydrating agent. Many wet gases can be dried by passage through a sulphuric acid bubbler provided the gases do not react with the acid. Sulphuric acid removes water from organic compounds as shown by its charring action on carbohydrates



Hot concentrated sulphuric acid is a moderately strong oxidising agent. In this respect, it is intermediate between phosphoric and nitric acids. Both metals and non-metals are oxidised by concentrated sulphuric acid, which is reduced to  $\text{SO}_2$ .



With zinc, which is a stronger reducing agent than copper, the reduction of concentrated sulphuric acid goes further to give sulphur or  $\text{H}_2\text{S}$ .

### 13.4.5 Uses of Sulphuric acid

Sulphuric acid is a prime industrial chemical. A nation's industrial strength can be gauged by the amount of sulphuric acid it produces and consumes. It is needed for the manufacture of hundreds of other compounds and also in many industrial processes. The bulk of sulphuric acid produced is used in the manufacture of fertilisers (e.g., ammonium sulphate, superphosphate). Other uses are in (a) petroleum refining, (b) manufacture of pigments, paints and dyestuff intermediates, (c) detergent industry, (d) metallurgical applications (e.g., cleansing metals before enamelling, electroplating and in the manufacture of batteries). Currently our country produces more than 2 million tonnes of sulphuric acid per annum compared to over 40 million tonnes produced in U.S.A and 120 million tonnes produced worldwide.

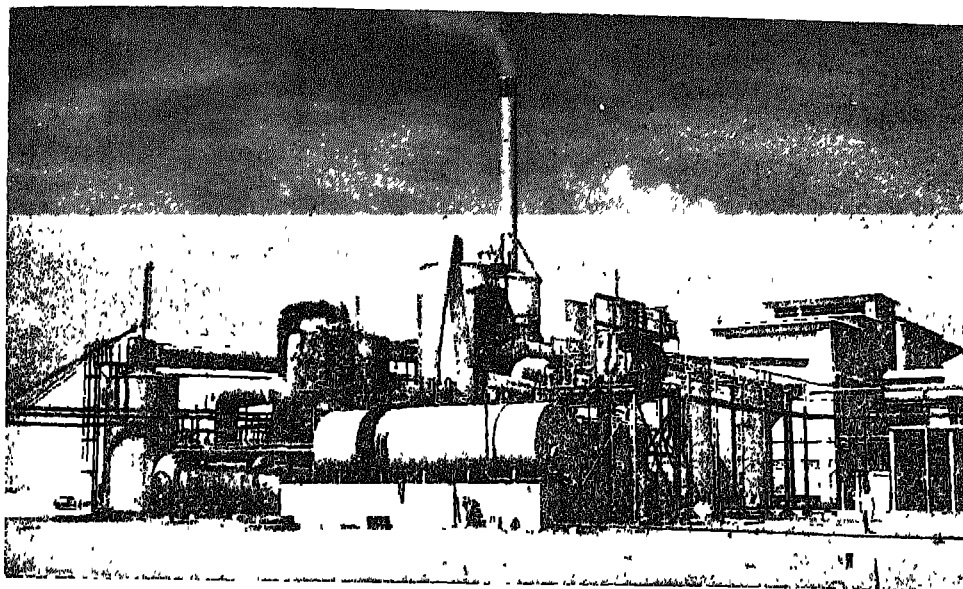
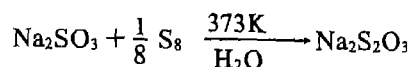


Photo III A sectional view of the chemical fertilizer plant (Parry's chemical fertilizer factory, Madras)

Courtesy PIB, New Delhi

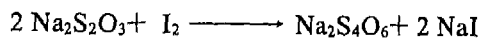
#### 13.4.6 Sodium Thiosulphate

If one of the oxygen atoms in the sulphate ion is replaced by sulphur, the resulting ion ( $\text{S}_2\text{O}_3^{2-}$ ) is known as THIOSULPHATE. The free acid,  $\text{H}_2\text{S}_2\text{O}_3$  is not stable but thiosulphate salts are stable and can be prepared by boiling aqueous solutions of metal sulphites with elemental sulphur



Hydrated sodium thiosulphate,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  is known as HYPO. It is used as a fixer in photography (Unit 15).

Thiosulphate is oxidised by iodine ( $\text{I}_2$ ) to tetrathionate. This reaction forms the basis for the iodometric titrations in volumetric analysis



Chlorine oxidises thiosulphate to sulphate in aqueous solution. Thiosulphate is therefore used as an 'anti-chlor' agent in the bleaching industry to remove the excess chlorine from textile fibres.

#### 13.5 HALOGENS

Group 17 of the periodic table comprises of the elements fluorine, chlorine, bromine, iodine and astatine. These elements are collectively known as the HALOGENS (Astatine)

is radioactive and occurs in nature only in traces. It is therefore of not any practical importance. The other elements occur extensively in nature in the form of halide salts. The name 'halogen' is derived from a Greek word which means *salt former*. Halogens and their compounds find extensive and varied uses in industry.

Each halogen has one electron less than the noble gas that follows it. Halogens are highly reactive elements. They readily accept a single electron to form uninegative ions or share their single unpaired electrons with other atoms to form covalent bonds. In line with this tendency, halogens exist as diatomic molecules under ordinary conditions. The melting and boiling points steadily increase from fluorine to iodine. Thus fluorine and chlorine are gases, bromine is a liquid and iodine is a solid. The physical and chemical properties of the halogens in their atomic and molecular states are shown in Table 13.1.

TABLE 13.1

## Atomic and Molecular Properties of Halogens

Property	F	Cl	Br	I
Valence electrons	$2s^2 2p^5$	$3s^2 3p^5$	$4s^2 4p^5$	$5s^2 5p^5$
Covalent radius (pm)	72	99	114	133
Ionic radius $E^-(\text{pm})$	133	184	196	220
Electron affinity ( $\text{kJ mol}^{-1}$ )	333	349	325	296
Ionisation energy ( $\text{kJ mol}^{-1}$ )	1681	1256	1143	1009
Electronegativity	4.0	3.0	2.8	2.5
Abundance, mol%	$2.8 \times 10^{-2}$	$2.6 \times 10^{-2}$	$8.5 \times 10^{-5}$	$4 \times 10^{-6}$
	$F_2$	$Cl_2$	$Br_2$	$I_2$
Melting point (K)	54	172	266	387
Boiling point (K)	85	239	333	458
Colour	Pale Yellow	Greenish Yellow	Dark Red	Purple Black
Bond energy ( $\text{kJ mol}^{-1}$ )	158.8	242.6	192.8	151.1
Bond distance (pm)	143	199	228	266

Because the halogens react readily by accepting an electron, they are all strong oxidising agents. The oxidising ability decreases from fluorine to iodine. Fluorine is the strongest oxidising agent among all the elements. It is the most electronegative element. In all its compounds it has an oxidation state of -1. Positive oxidation states exist for all other halogens.

## 13.5.1 Occurrence

Halogens are highly reactive and hence do not occur in the free elemental state in nature. They occur mainly in the form of  $X^-$  salts although iodine also occurs as iodate,

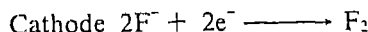
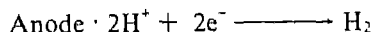
( $\text{IO}_3^-$ ) Chlorine is the most abundant of the halogens and its main commercial source is NaCl (common salt) occurring in sea water and rock beds. The sources of halogens and their abundance are shown below

Halogen	Abundance percentage in earth's crust	Main sources
Fluorine	0.07	Fluorospars ( $\text{CaF}_2$ ); fluorapatite [ $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ]
Chlorine	0.14	Sea water (2.8%), salt wells, salt beds ( $\text{NaCl}$ , $\text{KCl}$ , $\text{MgCl}_2$ , $\text{CaCl}_2$ )
Bromine	$2.5 \times 10^{-4}$	Sea water, salt lakes ( $\text{NaBr}$ , $\text{KBr}$ , $\text{MgBr}_2$ )
Iodine	$8 \times 10^{-6}$	Sea weeds (1-0.5% by weight), Chile salt peter (0.02% $\text{NaIO}_3$ )

### 13.5.2 Preparation

Because fluorine is the strongest chemical oxidising agent, the only practicable method of preparing it is by the electrolytic oxidation of hydrogen fluoride.

The electrolytic oxidation must be carried out under conditions (Can you guess why?) The reactions that occur at the cathode and anode are

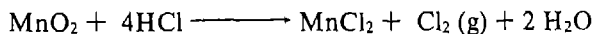


*Minimum electro negativity because Hydrogen and Fluorine combine*

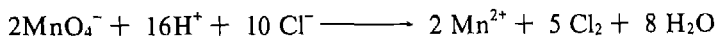
Since the electrolyte is highly corrosive and fluorine is extremely reactive, special care must be taken in selecting the material for construction of the cell. The electrolytic vessel is usually constructed of nickel, copper or Ni-Cu-Fe alloy known as Monel metal; these quickly become protected by the formation of a metal fluoride film. In industry, a mild-steel pot is used as the cathode. A carbon rod free from graphite is used as the anode. Since hydrogen and fluorine combine explosively, accidental mixing of the two gases must be avoided strictly. A diaphragm made of teflon is used to separate the cathode and the anode.

Industrial production of chlorine is carried out by electrolysis of natural brines or concentrated aqueous NaCl. Sodium hydroxide and hydrogen are also the products of this process. molten NaCl is used as the electrolyte, the co-product is sodium instead of sodium hydroxide (Unit 14).

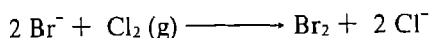
In the laboratory, chlorine can be prepared by the oxidation of HCl by manganese dioxide:



or by the treatment of sodium chloride in sulphuric acid solution with potassium permanganate.



Bromine is made by the oxidation of bromide ions in natural brine wells with  $\text{Cl}_2$ .

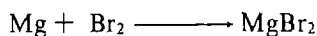
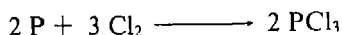
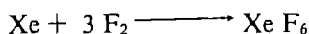


Iodine is commercially produced from sea weed which concentrates iodide ion from sea water. Burning of sea weed gives iodide ion which can be oxidised by chlorine as in the case of bromide oxidation.

### 13.5.3 Chemical Reactions of Halogens

Halogens combine directly with most metals and with some non-metals to give halides. Fluorine is the most reactive of all elements and forms compounds with all other elements under appropriate conditions except He, Ar and Ne.

The reactivity decreases in the order  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ . Some examples of the reaction of the halogens with metals and non-metals are shown below.

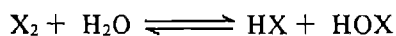


Halogens react with each other to produce a number of INTERHALOGEN COMPOUNDS,  $\text{X X}'_n$ , where  $n = 1, 3, 5, \text{ or } 7$ . The stability of these compounds increases as the size of the central atom increases. In these compounds, the smaller and more electronegative atom is assigned an oxidation state of  $-1$ , the central atom thus acquires a positive oxidation state. Some of the interhalogen compounds are shown below.

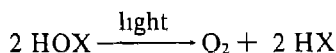
$\text{X X}'$	$\text{X X}'_3$	$\text{X X}'_5$	$\text{X X}'_7$
$\text{ClF}$	$\text{ClF}_3$	$\text{ClF}_5$	$\text{IF}_7$
$\text{BrF}$	$\text{BrF}_3$	$\text{BrF}_5$	
$\text{BrCl}$	$\text{IF}_3$	$\text{IF}_5$	
$\text{ICl}$	$\text{ICl}_3$		
$\text{IBr}$			

Can you try to work out the geometry of some of these compounds by applying the VSEPR theory?

Chlorine, bromine and iodine react with water to yield hydrohalic and hypohalous acid ( $\text{HX}$  and  $\text{HOX}$  respectively).



Fluorine reacts vigorously and instantaneously with water to yield  $\text{HF}$  and a variety of other products including  $\text{OF}_2$ .  $\text{HOX}$  has been isolated by fluorinating ice at  $-40^\circ\text{C}$ , it is extremely unstable and decomposes to give  $\text{HF}$  and  $\text{O}_2$ . Aqueous solutions of chlorine and bromine release oxygen when exposed to sunlight owing to the decomposition of  $\text{HOX}$ .

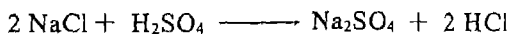




### 13.5.4 Hydrogen Halides

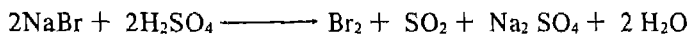
Halogens combine with hydrogen to form hydrogen halides, HX. The vigour of the reaction decreases from fluorine to iodine. Aqueous solutions of the hydrogen halides are known as hydrohalic acids.

Commercially hydrogen chloride and hydrogen fluoride are produced by the action of concentrated  $\text{H}_2\text{SO}_4$  on calcium fluoride (fluorspar) and sodium chloride respectively.



These reactions are the laboratory preparation of HF and HCl. In the acid industry but the presence of  $\text{SiO}_2$  leads to the formation of  $\text{H}_2\text{SiF}_6$  from which it is not easy to recover HF economically.

Treatment of bromides and iodides with concentrated sulphuric acid for the preparation of HBr and HI is not possible because they are oxidised by sulphuric acid to the respective halogens.



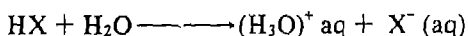
At room temperature, all the hydrogen halides are colourless gases with an irritating odour. There is a regular gradation in the melting and boiling points of the hydrogen halides. The boiling and melting points of HF are abnormally high because the molecules of HF are associated via hydrogen bonding. Some of the properties of hydrogen halides are shown in Table 13.2.

TABLE 13.2.

Properties of Hydrogen Halides

Property	HF	HCl	HBr	HI
Melting point(K)	190	158	186	222
Boiling point(K)	293	189	206	238
Bond length, (H-X) (pm)	91.7	127.4	141.4	160.9
Bond dissociation energy (kJ mol <sup>-1</sup> )	570	430	360	300

All the hydrogen halides are highly soluble in water and give hydrohalic acids. They are all strong acids except HF which is a weak acid in aqueous solution.



Their acidity increases in the order,  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$ . Salts of these acids are called halides, the most important of which is sodium chloride.

cmh

### 13.5.5. Uses of Halogens

Fluorine is used mainly for the manufacture of  $UF_6$  for nuclear power generation and  $SF_6$  for dielectrics. It is also used for the preparation of many fluorinating agents. The important organic chemicals derived from HF are the chlorofluorocarbons and tetrafluoroethylene (Teflon). Chlorofluorocarbons known as FREONS are used as refrigerants and in aerosols (Do you know what an aerosol is?). Teflon is a plastic which is not attacked by chemical reagents and is heat-resistant. It is used for many special applications. An important inorganic chemical made from HF is cryolite ( $Na_3AlF_6$ ) used for the production of aluminium. Minor uses of HF are in the glass industry as an etching agent and in the manufacture of fluoride salts. Prominent among the fluorides is NaF used for the fluoridation of water, one part per million level of fluoride in drinking water prevents tooth decay.

The chief uses of chlorine are

- (i) production of organic compounds (e.g., polyvinyl chloride, chlorinated hydrocarbons, pharmaceuticals, herbicides, pesticides);
- (ii) bleaching of paper, pulp and textiles and disinfectant for sterilising drinking water;
- (iii) production of inorganic compounds (e.g.,  $HCl$ ,  $PCl_3$ ,  $PCl_5$ , sodium hypochlorite ( $NaOCl$ ), bleaching powder ( $CaOCl_2$ )).

Bromine and Iodine are used to a much lesser extent than chlorine. The main outlet for bromine is ethylene bromide which is used as an additive to *leaded petrol*. Bromine is also used to make  $AgBr$  for photography.

Iodine is used as an antiseptic in the form of an alcoholic solution, which is known as TINCTURE OF IODINE. It is also used for the preparation of iodoform and potassium iodide. Iodide ion is necessary for the normal functioning of the thyroid gland. Insufficient iodide in the diet leads to GOITRE (enlargement of the thyroid gland). Hence sodium or potassium iodide is added to table salt and this type of salt is known as 'iodised' salt.

## 13.6. NOBLE GASES

The most characteristic property of the six elements of group 18 of the periodic table is their very low chemical reactivity. They are known as the NOBLE GASES. These elements come at the end of each period and have a full complement of electrons in their valence shells ( $1s^2$  or  $ns^2 np^6$ ). Gain or loss of electrons is not easy and therefore these elements do not form compounds with other elements readily. For a long time, the noble gases were regarded as inert and not capable of forming any compounds. However, since 1962 some compounds of xenon and krypton have been prepared.

### 13.6.1 Discovery of Noble Gases

The discovery of noble gases is an important landmark in the history of chemistry and the development of the periodic table. The existence of these elements were not foreseen by Mendeleev. Argon was discovered by Rayleigh in 1892 and confirmed by Ramsay in 1894. Ramsay passed nitrogen gas obtained from air over heated

ma am spe. small idied gas

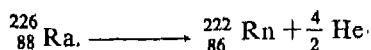
was named argon which in Greek means 'lazy'.

Prior to the discovery of argon, the existence of helium was recognised by Lockyer in 1868 from the spectrum of the sun's atmosphere. In 1895 Ramsay identified helium from the gases occluded in uranium minerals. By 1898, Ramsay and Travers isolated neon, krypton and xenon by careful fractionation of liquid air. The new elements were identified by their characteristic spectra. The last member of the group, radon, was spectroscopically detected by Dorn in 1901 and first isolated and studied by Rutherford and Soddy in 1902.

These unreactive gaseous elements could not be fitted into the Mendeleev's periodic table as they were not discovered during those days. After the discovery of these gases Ramsay made the bold suggestion that these elements constitute a whole new group to be placed between the halogens and the alkali metals. This suggestion was proved correct later.

### 13.6.2 Occurrence and Isolation of Noble Gases

Except radon all the noble gases occur in the atmosphere. Their total abundance in dry air is ~ 1% by volume. The main component is argon (Table 13.3). Neon, argon, krypton and xenon are obtained as byproducts of liquefaction of air and separation of its constituents by fractional distillation and condensation cycles. The main commercial source of helium is natural gas. Helium is the second most abundant element in the universe (23% compared to 76% hydrogen) although its terrestrial abundance is very low. Radon is obtained as a decay product of  $^{226}\text{Ra}$ .



### 13.6.3 Physical Properties of the Noble Gases

All the noble gases are monoatomic. They are colourless, odourless and tasteless. They are sparingly soluble in water. The physical properties of these compounds vary regularly from helium to radon. Some of the properties are shown in Table 13.3.

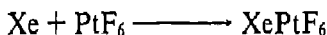
TABLE 13.3.  
Some Properties of Noble Gases

Element	Abundance in air by volume (ppm)	Boiling point (K)	Melting point (K)	First ionisation energy (kJ mol <sup>-1</sup> )	Atomic radius (pm)
He	5.2	4	a	2372	93
Ne	18.2	27	25	2080	112
Ar	93.4	87	84	1520	154
Kr	1.1	120	116	1351	167
Xe	0.09	165	161	1170	190
Rn	trace	211	202	1037	—

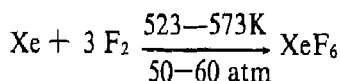
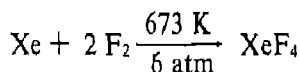
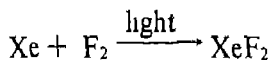
a cannot be frozen without applying pressure

### 13.6.4 Chemistry of Noble Gases

We have already noted the extremely low chemical reactivity of the noble gases. For many years, noble gas compounds proved elusive. In 1962, Bartlett prepared the first noble gas compound,  $\text{XePtF}_6$  by reacting Xe with  $\text{PtF}_6$ . Since then a number of xenon compounds have been prepared. Invariably all the compounds contain



fluorine or oxygen attached to xenon. The more important of these compounds are the xenon fluorides  $\text{XeF}_n$  ( $n = 2, 4$  or  $6$ ) which are obtained by direct combination of the elements at  $673 \text{ K}$  in a sealed nickel container.  $\text{XeF}_2$  can also be prepared by irradiating a mixture of xenon and fluorine with sunlight or light from a high pressure mercury arc lamp



$\text{XeF}_2$  has a linear structure;  $\text{XeF}_4$  is square planar.  $\text{KrF}_2$  is also known but no stable compounds of He, Ne or Ar are known

### 13.6.5. Uses of Noble Gases

Argon is used mainly to provide an inert atmosphere in high temperature metallurgical processes (arc-welding of metals or alloys) and for filling electric bulbs. It is also used in the laboratory for handling substances that are air-sensitive.

Helium is non-flammable and light. Hence helium is used in filling balloons for meteorological observations. It is also used in gas-cooled nuclear reactors. Liquid helium finds use as cryogenic agent for carrying out various experiments at low temperatures. Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes. There are no significant uses of xenon and krypton. They are used in light bulbs designed for special purposes (e.g., flash bulbs, electronic flashes for photography).

## EXERCISES

- 13.1 Describe briefly the different methods of obtaining elemental boron
- 13.2 Why do boron halides form 'addition compounds' with amines?
- 13.3 Write the structure of diborane.
- 13.4 Why are boron halides and diborane referred to as electron deficient compounds?
- 13.5 Describe briefly the chemical reactions of boron with oxygen, halogens and nitrogen
- 13.6 What happens when a borax solution is acidified? Write a balanced equation for the reaction
- 13.7 Describe what happens when boric acid is heated
- 13.8 Why does not silicon form an analogue of graphite?
- 13.9 What is the importance of elemental silicon of high purity? How is it obtained?
- 13.10 What is carborundum? What is its common use?
- 13.11 Explain why silicon shows a higher covalency than carbon
- 13.12 How do the following substances differ?  
(Quartz, ordinary soda glass, pyrex glass)
- 13.13 For a compound  $\text{LiAl}(\text{SiO}_3)_2$ , what is the charge on the  $\text{SiO}_3$  unit? What is the arrangement of oxygen atoms around the silicon atom?
- 13.14 Why does not elemental phosphorus exist as  $\text{P}_2$  under ordinary conditions?
- 13.15 Explain the difference in the structures of white and red phosphorus
- 13.16 Describe a method for the isolation of phosphorus from  $\text{Ca}_3(\text{PO}_4)_2$ .
- 13.17 Write the structures of orthophosphoric acid, phosphate ion and linear trimetaphosphate ion.
- 13.18 How is pyrophosphoric acid related to orthophosphoric acid?
- 13.19 Name a few phosphatic fertilisers and briefly describe methods of their manufacture
- 13.20 Discuss the allotropy of sulphur
- 13.21 Write resonance structures for the following  
 $\text{SO}_4^{2-}$ ,  $\text{O}_3$ ,  $\text{PO}_4^{3-}$
- 13.22 Starting from elemental sulphur, how would you prepare  
(i)  $\text{H}_2\text{SO}_4$  (ii)  $\text{SCL}_2$ , (iii)  $\text{Na}_2\text{S}_2\text{O}_3$ .
- 13.23 Describe the contact process for the manufacture of sulphuric acid.
- 13.24 Give an example of a reaction in which  $\text{H}_2\text{SO}_4$  behaves as  
(i) a strong acid  
(ii) a dehydrating agent  
(iii) an oxidising agent
- 13.25 Write the products of the following reactions:  
(i)  $\text{Cu} + \text{Conc. H}_2\text{SO}_4 \longrightarrow$

- (ii)  $\text{H}_2\text{S} + \text{SO}_2 \xrightarrow{\text{Catalyst}}$   
 (iii)  $\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \longrightarrow$
- 13.26 Give a method of preparation of each of the following halogens:  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$  and  $\text{I}_2$
- 13.27 How would you prepare  
 (i)  $\text{HF}$  from  $\text{CaF}_2$ , (ii)  $\text{Br}_2$  from sea water,  
 (iii)  $\text{I}_2$  from  $\text{NaIO}_3$ , and (iv)  $\text{HBr}$  from  $\text{NaBr}$ ?
- 13.28 Give examples of a few interhalogen compounds of type  $\text{XX}_n$  ( $n = 3, 5, 7$ ) and predict their molecular shapes from VSEPR theory.
- 13.29 Write the products of the following relations. Give balanced equations.  
 (i)  $\text{P} + \text{Cl}_2 \longrightarrow$   
 (ii)  $\text{Br}^- + \text{Cl}_2 \longrightarrow$   
 (iii)  $\text{MnO}_2 + \text{HCl} \longrightarrow$   
 (iv)  $\text{Cl}_2 + \text{H}_2\text{O} \longrightarrow$   
 (v)  $\text{NaBr} + \text{H}_3\text{PO}_4 \longrightarrow$
- 13.30 Describe the chief uses of chlorine, fluorine and their compounds
- 13.31 Describe briefly the discovery of noble gases.
- 13.32 What are the chief uses of the noble gases helium, neon and argon?
- 13.33 What are the molecular shapes of  $\text{XeF}_2$  and  $\text{XeF}_4$ ?
- 13.34 How do  $\text{NO}_3^-$  and  $\text{PO}_3^-$  differ structurally?
- 13.35 Explain why  $\text{CO}_2$  is a gas whereas  $\text{SiO}_2$  is a high melting solid
- 13.36 Describe the commercial uses of sulphuric acid.
- 13.37 What are the oxidation states of sulphur in the following compounds:  
 (i)  $\text{PbS}$ , (ii)  $\text{SO}_2$ , (iii)  $\text{SO}_4^{2-}$ , (iv)  $\text{SCl}_2$ .

## UNIT 14

### CHEMISTRY OF LIGHTER METALS

*Most of the elements in the periodic table are metals.*

1																18
	2															
Na	Mg															
K	Ca															

#### OBJECTIVES

In this Unit, we shall learn:

- \* the chemistry of a few of the lighter elements (sodium, potassium, magnesium, calcium and aluminium);
- \* the chemistry of some common compounds of these metals;
- \* the manufacture of industrially useful compounds of these metals such as soda ash, caustic soda, lime and cement;
- \* the biological significance of the cations  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ .

THE ALKALI METALS (e.g., sodium, Na and potassium, K) and the alkaline earth metals (e.g., magnesium, Mg and calcium, Ca) are located in the left-hand side of the periodic table. These elements exhibit metallic properties and because of their low density, they are called lighter metals. These metals form many compounds which we use in our daily life, the most common being common salt, soda ash, baking soda and lime. Monovalent sodium and potassium ions and bivalent magnesium and calcium ions are found in large proportions in biological fluids. These ions perform important biological functions such as maintenance of ion balance and nerve conduction. Aluminium, Al is the second member of group 13 in the periodic table. It forms many useful alloys with other metals.

### 14.1 SODIUM AND POTASSIUM

Sodium and potassium belong to group 1 of the periodic table. The other elements of this group are lithium, Li, rubidium, Rb, caesium, Cs, and francium, Fr. These metals are reactive and they form univalent ions. Their compounds are generally ionic. Some of the important general properties of these elements are given in Table 14.1

These elements are strongly electropositive. The ionisation energies of the alkali metals are by far the lowest compared to the elements of the other groups. The monovalent cations of sodium and potassium have the stable inert gas configuration. It is easy to excite the valence electrons of these metals to higher energy states when the excited electrons return to the ground state, there is emission of radiation in the visible region (e.g., yellow for sodium and lilac for potassium). Alkali metals can, therefore, be detected by their flame tests.

TABLE 14.1  
Some General Properties of Sodium and Potassium

Element	Atomic number	Electronic Configuration	Atomic Radius (pm)	Ionic Radius $M^+(pm)$	$m p$ (K)	$b p$ (K)	Ionisation energy ( $kJ\ mol^{-1}$ )	Density ( $g\ cm^{-3}$ )
Sodium (Na)	11	[Ne]3s <sup>1</sup>	186	95	370.8	1155.9	495	0.97
Potassium (K)	19	[Ar] 4s <sup>1</sup>	227	133	336.8	1039	418	0.86

For a flame test, take a sodium or potassium salt (e.g., NaCl, KCl) on a metallic spatula. Heat the tip of the spatula in a flame and notice the colour of the flame.

#### 14.1.1 Occurrence and Extraction

Sodium and potassium occur widely in nature. The relative abundance of sodium and potassium in the earth's crust is nearly 2.5% and 1.8% respectively, (sea water is a rich source of sodium and potassium). A common mineral containing sodium is ALBITE (soda feldspar),  $NaAlSi_3O_8$ , which is one of the main constituents of rocks. In



addition, sodium occurs as rock salt ( $\text{NaCl}$ ) deposits, SALT PETRE ( $\text{NaNO}_3$ ) and in many clays. Potassium chloride ( $\text{KCl}$ ) occurs in nature only to a limited extent. The double salt CARNAITE  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  is found in large quantities. Potassium also occurs abundantly as POTASSIUM FELDSPAR,  $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ .

Alkali metals are strong reducing agents and hence cannot be isolated by reduction of their oxides or other compounds. Sodium and potassium are therefore generally obtained by electrolytic reduction of their molten chlorides. The melting points of chlorides of sodium and potassium are high and in order to lower their melting points, calcium chloride ( $\text{CaCl}_2$ ) is added. The isolation of sodium metal is carried out in a Down's cell as shown in Figure 14.1. Sodium chloride (40%) is mixed with calcium chloride (60%) and the molten mixture is electrolysed at about 850 K using a carbon (graphite) anode and an iron (steel) cathode.

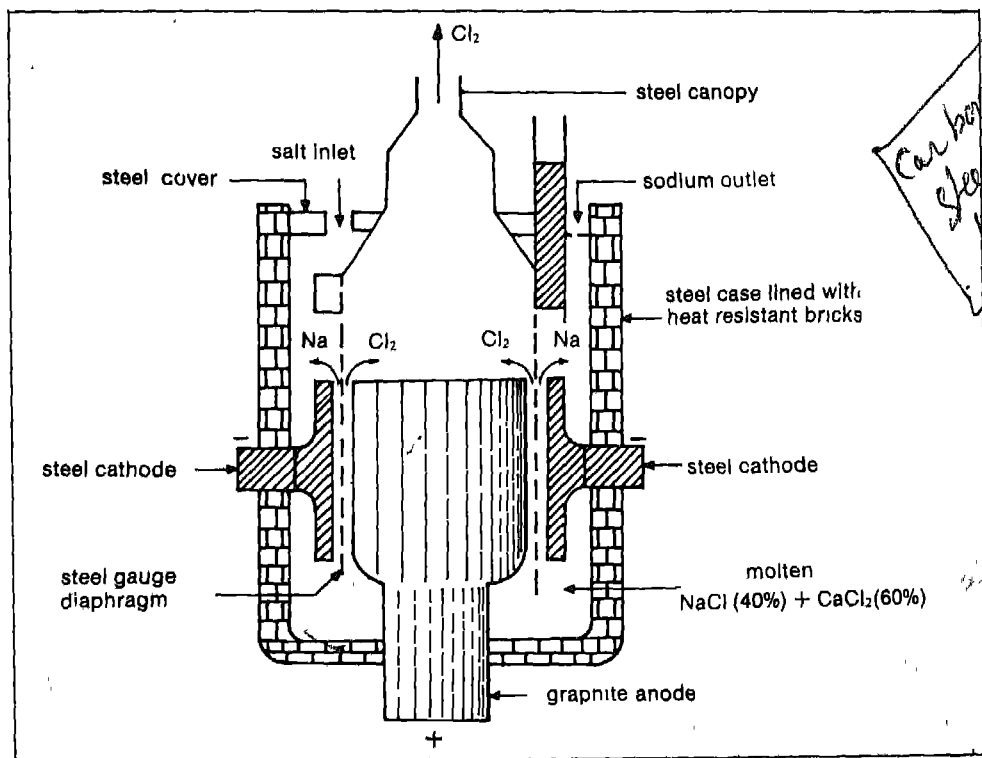


Fig. 14.1 Down's Cell for manufacture of sodium

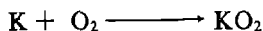
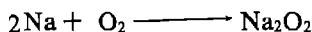
Potassium is also obtained by electrolysis. The electrolyte employed for the isolation of potassium metal is fused potassium hydroxide ( $\text{KOH}$ ).

#### 14.1.2 Properties of Sodium and Potassium

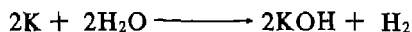
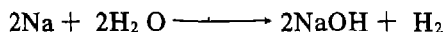
Sodium and potassium are light, soft metals with silvery white lustre. The densities

of sodium and potassium are  $0.97 \text{ g/cm}^3$  and  $0.86 \text{ g/cm}^3$  respectively. Sodium metal can be cut easily with a knife. Its surface when freshly cut is shining but is often covered with a layer of the oxides or the carbonate formed by contact with air. Sodium and potassium metals are extremely reactive and they are kept under kerosene to prevent the metals from exposure to oxygen and moisture. Potassium is more reactive than sodium. Small pieces of potassium sometimes melt and catch fire spontaneously in air.

Sodium reacts vigorously with oxygen to form sodium peroxide,  $\text{Na}_2\text{O}_2$  while potassium burns in air to combine with oxygen to form potassium superoxide,  $\text{KO}_2$



Both sodium and potassium react violently with water to form their respective hydroxides liberating hydrogen gas.



#### 14.1.3 Uses

Alkali metals such as sodium and potassium are most commonly used as reducing agents. Amalgams of sodium and potassium with mercury find extensive use in the preparation of organic compounds. Liquid sodium or its alloy with potassium is employed as a coolant in nuclear reactors. Sodium-lead alloy is used in the preparation of tetraethyl lead ( $\text{Pb}(\text{C}_2\text{H}_5)_4$ ), which is an antiknock agent in petrol.

#### 14.1.4 Some important Compounds of Sodium and Potassium

Sodium and potassium form many industrially important compounds, for example, halides, carbonates, sulphates and hydroxides of sodium and potassium. In general, the compounds of sodium and potassium are ionic in nature and are readily soluble in water.

##### *Sodium Chloride, $\text{NaCl}$*

Sea water contains about 3.5% of soluble salts, the most common of which is sodium chloride (2.7 to 2.9%). In tropical countries like India, common salt is generally obtained by evaporation of sea water. India has long coastal line. Approximately 50 lakh tons of salt are produced annually in India by solar evaporation. The coastal line of Gujarat is one of the important areas in the country producing salt. The hot, dry, windy climate leads to fast evaporation of water from the artificial ponds containing sea water. Crude sodium chloride, generally obtained by crystallisation of brine contains sodium sulphate, calcium sulphate, calcium chloride and magnesium chloride as impurities. Calcium chloride,  $\text{CaCl}_2$ , and magnesium chloride,  $\text{MgCl}_2$  are undesirable impurities because they are deliquescent (absorb moisture).

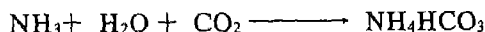
easily from the atmosphere). To obtain pure sodium chloride, the crude salt is dissolved in minimum amount of water and filtered to remove insoluble impurities. The solution is then saturated with hydrogen chloride gas. Crystals of pure sodium chloride separate out. Calcium and magnesium chlorides, being more soluble than sodium chloride, remain in solution.

Sodium chloride melts at 1081 K. It has a solubility of 36.0 g in 100 g of water at 273 K. The solubility does not increase appreciably with increase in temperature.

### Sodium Carbonate (Soda Ash), $\text{Na}_2\text{CO}_3$

Sodium carbonate is made by the Solvay process. This process consists of many reactions. It takes place in several stages. The raw materials used in the process are common salt and limestone. Calcium chloride is a by-product in this process. The diagram in Fig. 14.2 shows this process.

(i) Carbon dioxide is passed under pressure into a strong sodium chloride (brine) solution already saturated with ammonia. Carbon dioxide forms carbonic acid which neutralises ammonia and forms ammonium hydrogen carbonate



(ii) Addition of common salt ( $\text{NaCl}$ ) to the solution containing all the ions,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$  and  $\text{HCO}_3^-$ , precipitates out the least soluble  $\text{NaHCO}_3$  which is filtered off.

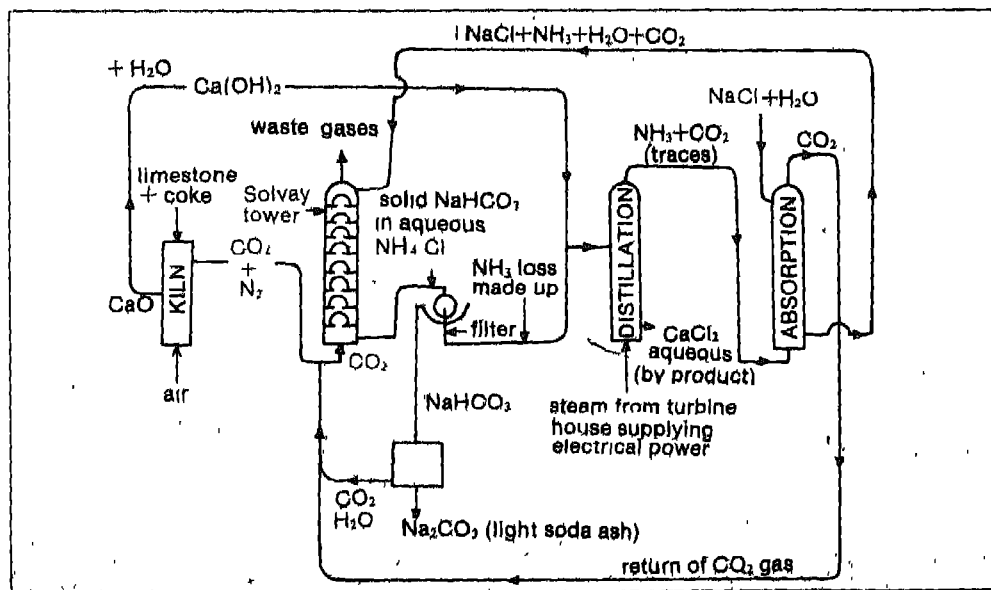
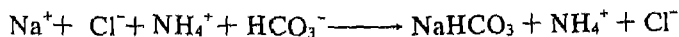


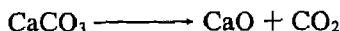
Fig. 14.2 Solvay process for sodium carbonate

(iii) Sodium hydrogen carbonate is heated to convert it to sodium carbonate

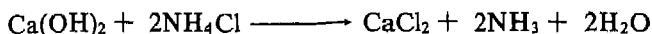


The  $\text{CO}_2$  evolved is useful (recirculated) for step (i).

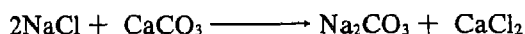
(iv) Carbon dioxide in step (i) is generally obtained by heating limestone,  $\text{CaCO}_3$ .



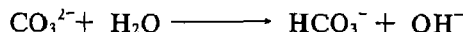
(v) Quick lime ( $\text{CaO}$ ) in step (iv) is slaked with water and boiled with ammonium chloride produced in step (ii) to liberate ammonia which is used in step (i).



(vi) The overall reaction is.



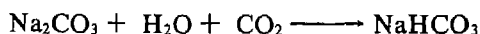
Sodium carbonate is readily soluble in water and the crystals obtained from the solution are of the decahydrate,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ . This is known as WASHING SODA. The name 'washing soda' is derived because of its use in water softening. Large quantities of this compound are used in the glass industry. On heating the decahydrate loses the water of crystallisation to form the monohydrate,  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ . Above 373 K, the monohydrate becomes an anhydrous white powder. Sodium carbonate is an inexpensive alkali. It hydrolyses in water to give an alkaline solution.



*Sodium Hydrogen Carbonate (Baking Soda),  $\text{NaHCO}_3$*

Sodium hydrogen carbonate is known as baking soda because it decomposes on heating to generate bubbles of carbon dioxide (leaving holes in cakes or pastries and making them light and fluffy).

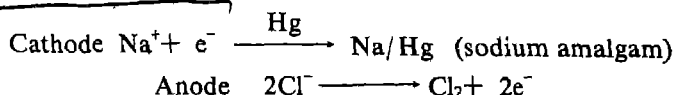
For household purpose,  $\text{NaHCO}_3$  is made by saturating a solution of sodium carbonate with carbon dioxide. The white crystalline powder of sodium hydrogen carbonate gets separated being less soluble.



Sodium hydrogen carbonate is a mild antiseptic for skin infections.

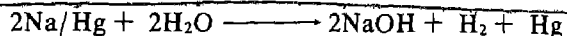
*Sodium Hydroxide (Caustic Soda),  $\text{NaOH}$*

Sodium hydroxide is made from sodium chloride by electrolysis. A brine solution is electrolysed using a mercury cathode and a carbon anode for this purpose. Sodium metal discharged at the cathode combines with mercury to form sodium amalgam. Chlorine gas is evolved at the anode.



The sodium amalgam is continually pumped into a separate chamber, where it is

brought into contact with water to give sodium hydroxide and hydrogen gas,



Because of its high reactivity, stringent steps are taken to keep the sodium amalgam and chlorine apart. The Castner-Kellner cell for the manufacture of caustic soda is shown in Fig. 14.3.

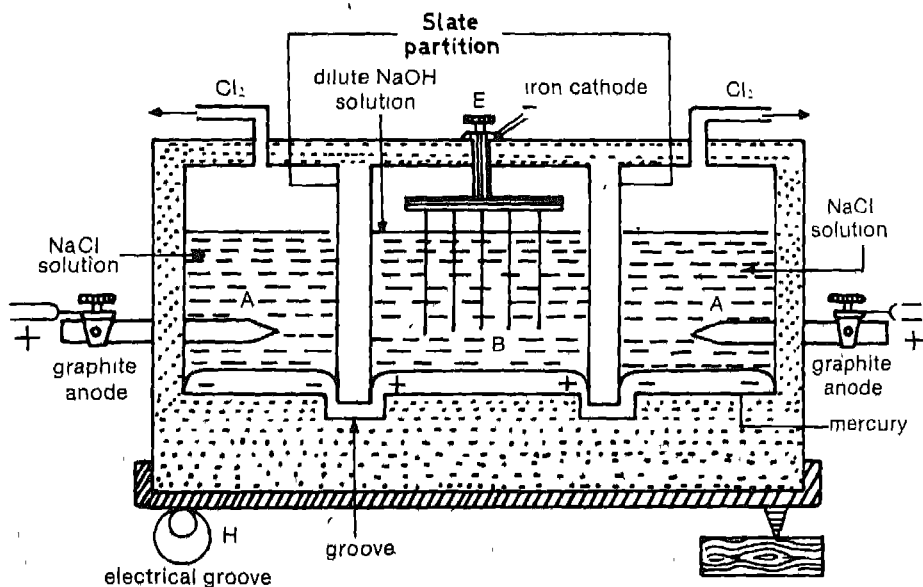


Fig. 14.3 Castner-Kellner Cell for manufacture of sodium hydroxide

You will notice that in this method, a small quantity of mercury dissolves in the spent brine solution and this is usually allowed to flow into the sea or river. Mercury is poisonous for both fish and man. Effective steps have to be taken to check this undesirable environmental pollution.

Sodium hydroxide is a white, translucent solid. It melts at 591 K. It is readily soluble in water to give a strongly alkaline solution. Crystals of sodium hydroxide are deliquescent. The sodium hydroxide solution formed at the surface reacts with the  $\text{CO}_2$  in the atmosphere to form a crust of  $\text{Na}_2\text{CO}_3$ .

Sodium hydroxide is a strong alkali and is used widely in the chemical industry, e.g., soap manufacture, purification of bauxite, manufacture of rayon. However, when a base is required to neutralise acids, it is more economical to use sodium carbonate, ammonia or lime. The chlorine gas which is a valuable by-product can be used for the production of chemicals such as polyvinyl chloride (PVC), an important plastic (Unit 13).

### Potassium Chloride, KCl

Potassium salts are important fertilisers. The fertiliser industry refers to any potassium salt as 'potash'. The main salts used as fertilisers are KCl,  $\text{KNO}_3$  and  $\text{K}_2\text{SO}_4$ . Potassium salts are obtained from sea water. A semi-commercial plant for potassium chloride from sea biterrens has been set up in Kandala (Gujarat).

Potassium chloride is a colourless crystalline solid. It has a melting point of 1063K.

### Potassium Hydroxide, KOH

Potassium hydroxide, KOH is prepared by the electrolysis of potassium chloride solution or by the treatment of potassium carbonate with lime. Potassium hydroxide is purified by dissolving it in alcohol. It is a white crystalline solid. It has a m.p. of 633K. It is readily soluble in water.

## 14.2 MAGNESIUM AND CALCIUM

Magnesium and calcium belong to group 2 elements in the periodic table. The other elements in the group are beryllium (Be), strontium (Sr), barium (Ba) and radium (Ra). These elements have two electrons in the outermost shell with the general electronic configuration of  $ns^2$ . Some general properties of these elements are given in Table 14.2.

Table 14.2

Some General Properties of Magnesium and Calcium

Element	Atomic number	Electronic configuration	Atomic radius (pm)	Ionic radius $M^{2+}$ (pm)	m.p. (K)	b.p. (K)	Ionisation energy ( $\text{kJ mol}^{-1}$ )		Density ( $\text{g cm}^{-3}$ )
							I	II	
Magnesium (Mg)	12	$[\text{Ne}]3s^2$	136	65	924	1363	738	1450	1.7
Calcium (Ca)	20	$[\text{Ar}]4s^2$	174	99	1123	1765	590	1146	1.6

The first ionisation energies of group 2 elements are higher than those of the corresponding group 1 elements. This is because the atoms of group 2 elements are smaller in size (compare the atomic radii with Na and K) and the electrons are more tightly bound. The second ionisation energies are almost twice the first ionisation energies in these elements. This indicates that more energy has to be spent to remove the electron from the monovalent ion. Magnesium and calcium form divalent cations, but they are less electropositive than the alkali elements. In view of the smaller size of the atoms and ions, alkaline earth metals are denser and harder than the alkali metals and have higher melting points.

### 14.2.1 Occurrence and Extraction

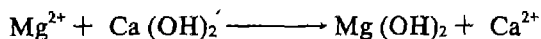
Magnesium and calcium are among the most abundantly found elements in the

earth's crust (magnesium and calcium occupy the sixth and third positions in the order of abundance). The chief minerals of magnesium are CARNALITE,  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ; MAGNESITE,  $\text{MgCO}_3$  and silicious materials such as TALC,  $\text{H}_2\text{Mg}(\text{SiO}_3)$  and ASBESTOS,  $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ . Magnesium content in sea water is about 0.13%, but it is sufficient to make its recovery economical. Magnesium occurs as chlorophyll in plants. Calcium occurs as carbonate,  $\text{CaCO}_3$  in MARBLE, CHALK and LIMESTONE. A few important minerals of calcium are DOLOMITE ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ ), ANHYDRITE ( $\text{CaSO}_4$ ), GYPSUM, ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), FLUORSPAR, ( $\text{CaF}_2$ ), and HYDROXY APATITE,  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ . In addition, calcium is an important constituent of many sea shells and corals.

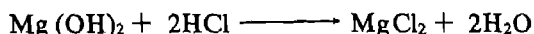
Calcium and magnesium metals are strong reducing agents. They cannot be obtained in the metallic form by chemical reduction. They are obtained by electrolysis of their fused anhydrous salts.

Magnesium from sea water is obtained by the Dow process. In this process, molten magnesium chloride is electrolysed using an iron cathode and a carbon anode. The process consists of the following steps

(i) Magnesium ion is precipitated as magnesium hydroxide by the addition of slaked lime,  $\text{Ca}(\text{OH})_2$  to the sea water



(ii) Magnesium hydroxide is converted to the chloride by treatment with hydrochloric acid.

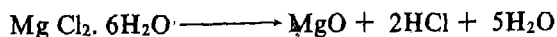


The chloride is crystallised as  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ .

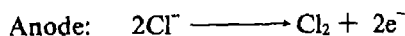
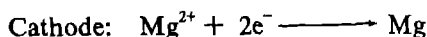
(iii) Fused magnesium chloride for electrolysis is obtained as follows:

Magnesium chloride is partially dehydrated by passing a current of dry hydrogen chloride gas. The chloride thus obtained is added to a molten mixture of sodium chloride and calcium chloride (temp. range 973-1023K). Magnesium chloride melts under this condition with the loss of water

If magnesium chloride hydrate is heated strongly, it hydrolyses to yield magnesium oxide (magnesia) which is a refractory

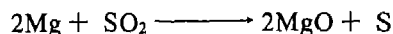
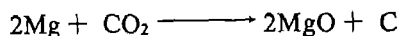


(iv) The molten mixture of  $\text{MgCl}_2$ ,  $\text{NaCl}$  and  $\text{CaCl}_2$  is electrolysed. Magnesium is formed at the cathode and chlorine is evolved at the anode. The chlorine is used to make hydrochloric acid which in turn is required for making magnesium chloride.



### 14.2.2 Properties of Magnesium and Calcium

Magnesium is a metal of low density. It burns in air or oxygen with a brilliant flame. The products of burning in air are magnesium oxide and magnesium nitride ( $\text{Mg}_3\text{N}_2$ ). Magnesium burns with the evolution of much heat (more heat per mole than even hydrogen). It also burns in many other gases as well, such as  $\text{CO}_2$  and  $\text{SO}_2$  forming  $\text{MgO}$ .



### 14.2.3 Uses

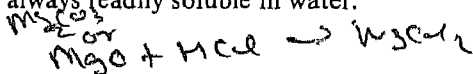
Magnesium being a light metal forms many alloys with aluminium, zinc, manganese and tin. Magnesium-aluminium alloys are used in aircraft construction. Magnesium (powder and ribbon) is used in flash powders and bulbs. A suspension of magnesium hydroxide in water (called milk of magnesia) is used as an antacid when a person suffers from excess acidity. Magnesium carbonate is an ingredient of tooth pastes.

Calcium is a powerful reducing agent. It is used in the extraction of metals from oxides (which are difficult to reduce with carbon). Calcium exhibits high reactivity towards oxygen and nitrogen. Because of this, calcium is used to remove air from vacuum tubes.

### 14.2.4 Some Important Compounds of Magnesium and Calcium

Magnesium and calcium form divalent ions. They form compounds with many non-metals. The compounds are generally ionic. Unlike the salts of alkali metals, those of magnesium and calcium are not always readily soluble in water.

#### Magnesium Chloride, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$



The main source of magnesium chloride is carnallite deposits. Another source is sea water. In the laboratory, it is prepared by the action of hydrochloric acid on magnesium oxide or carbonate. It crystallises as a hexahydrate,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . Water molecules in this hydrate are removed by heating it in a stream of hydrogen chloride gas.

A saturated solution of magnesium chloride when mixed with magnesium oxide sets to a hard mass. This has the composition  $\text{MgCl}_2 \cdot 5\text{MgO} \cdot x\text{H}_2\text{O}$ . This is used as MAGNESIA CEMENT.

#### Magnesium Sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

Magnesium sulphate, occurs as the mineral KIESERITE,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , or as EPSOMITE SALT,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , in the mineral waters of the Epsom spring in England. In the laboratory, it is prepared by treating magnesium metal, magnesia ( $\text{MgO}$ ) or magnesium carbonate with dilute sulphuric acid. Magnesium sulphate is used in medicine as a purgative and as a mordant for cotton goods in the dyeing industry.

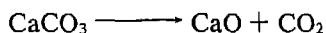


Magnesium ions in solution can be tested for by the phosphate test. Disodium hydrogen phosphate,  $\text{Na}_2\text{HPO}_4$ , is used as the reagent ✓

### Calcium Oxide, $\text{CaO}$

Calcium oxide, known as quicklime is a primary material of importance in the building industry. Its utility lies in the fact that it is the cheapest form of alkali.

It is made on a commercial scale by heating limestone in a rotatory kiln at 1070-1270 K.

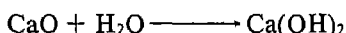


Calcium oxide is a white amorphous solid. It has a m.p. of 2870 K. On exposure to atmosphere, it absorbs moisture and carbon dioxide

Calcium oxide is extensively used in chemical industries. For example, it is used in the purification of sugar and in the manufacture of dyestuffs

### Calcium Hydroxide, $\text{Ca}(\text{OH})_2$

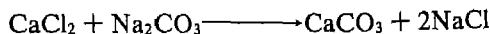
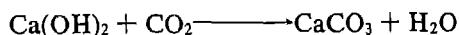
Calcium hydroxide, is known as SLAKED LIME. Addition of water to quicklime produces slaked lime



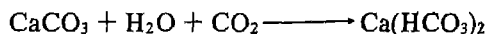
Calcium hydroxide is a white amorphous powder. It is sparingly soluble in water. A suspension of slaked lime in water is called MILK OF LIME

### Calcium Carbonate, $\text{CaCO}_3$

Calcium carbonate occurs in nature in several forms Limestone and marble are two of them. It can be prepared by passing carbon dioxide through slaked lime or by the addition of sodium carbonate to calcium chloride.



Excess of carbon dioxide should be avoided since this leads to the formation of calcium hydrogen carbonate.



Calcium carbonate, is a white fluffy powder. It is almost insoluble in water. Calcium carbonate  $\text{CaCO}_3$  along with  $\text{MgCO}_3$  is used in the extraction of metals such as iron ✓

### Calcium Sulphate, $\text{CaSO}_4$

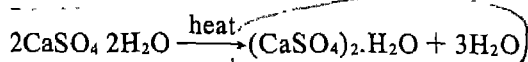
In nature calcium ~~sulphate~~ occurs as the anhydride,  $\text{CaSO}_4$ , or as the dihydrate, gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . Large quantities of gypsum are available in India in the states

of Punjab and Rajasthan.

In the laboratory, it is prepared by the action of sulphuric acid on  $\text{CaCl}_2$ . The dihydrate is sparingly soluble in water.

Interesting observations have been recorded during the heating of gypsum. Initial heating changes its crystal structure. On further heating at 390 K, it loses water and forms  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  or  $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$ . This is known as PLASTER OF PARIS. On heating above 437 K, it becomes anhydrous  $\text{CaSO}_4$  and does not set when mixed with water. It is known as DEAD BURNT PLASTER.

Plaster of Paris. It is a hemihydrate of calcium sulphate. It is formed by the partial dehydration of calcium sulphate dihydrate (gypsum) by heating in a kiln to 393–403 K with agitation.



Plaster of Paris has the remarkable property of setting and hardening when it is mixed with sufficient water to form a slurry of a suitable consistency. A hard crystalline mass of gypsum is formed.

The largest use of Plaster of Paris is in the building industry as well as plasters and wall boards which are commonly made by hydration of mixtures of lime and calcium sulphate hemihydrate often with a fibre base. It is used for making decorative materials as well. Plaster of Paris is used for immobilising the affected part of organs when there is bone fracture or sprain.

### 14.3 ALUMINIUM

Aluminium is one of the elements of group 13 of the periodic table. The other elements are boron (B), gallium (Ga), indium (In) and thallium (Tl). These elements have three electrons in the outermost shell,  $ns^2np^1$ . They form tripositive ions. These elements are less electropositive than alkali and alkaline earth metals of groups 1 and 2. Some of the general properties of aluminium are given in Table 14.3.

TABLE 14.3

Some General Properties of Aluminium

Element	Atomic number	Electronic configuration	Atomic radius (pm)	Ionic radius $M^{3+}$ (pm)	$m.p.$ (K)	$b.p.$ (K)	Ionisation energy ( $\text{kJ mol}^{-1}$ )			Density ( $\text{g cm}^{-3}$ )
							I	II	III	
Aluminium (Al)	13	$[\text{Ne}] 3s^2 3p^1$	125	50	933	2743	600	2427	3658	2.70

Aluminium has a high first ionisation energy and tends to form more covalent compounds. Although aluminium is a reactive metal according to the electrochemical series, it is rendered unreactive because of the presence of a stable oxide film on its surface.

### 14.3.1 Occurrence and Extraction

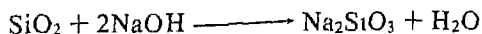
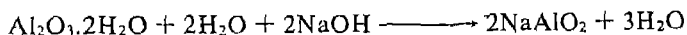
Aluminium occurs widely as a constituent of rocks and soils. It is the most abundant element (8.1% by weight) in the earth's crust after oxygen and silicon.

The important minerals of aluminium are BAUXITE hydrated aluminium oxides generally represented as  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , LEPIDOLAR,  $\text{KAlSi}_3\text{O}_8$ ; CRYOLITE  $\text{Na}_3\text{AlF}_6$  and MICA  $\text{KAlSi}_3\text{O}_{10}(\text{OH})_2$ . In India, mica is found in Katni, Belgaum, places near Jammu, Rewa and Orissa. India is the largest supplier of mica. It is found in Bihar, Madhya Pradesh, Maharashtra, Tamil Nadu as well as Jammu and Kashmir.

Extraction of aluminium from bauxite involves two stages. In the first stage, pure alumina ( $\text{Al}_2\text{O}_3$ ) is obtained from bauxite and in the second stage electrolysis of molten alumina is carried out to give aluminium metal.

(i) Bauxite is treated with a hot concentrated solution of sodium hydroxide. Aluminium dissolves to form sodium aluminate,  $\text{NaAlO}_2$ , leaving behind iron oxide which is present as an impurity.

This is a simplified picture of aluminate formation. Actually the chemistry of aluminates is complex. Aluminium hydroxide which is formed redissolves in excess of sodium hydroxide to form sodium aluminate,  $\text{NaAl}(\text{OH})_4$ . This is not very stable and on heating gets converted to  $\text{NaAlO}_2$  which is called sodium meta-aluminate. Along with the aluminate solution, silica,  $\text{SiO}_2$  also dissolves in sodium hydroxide to form soluble sodium silicate,  $\text{Na}_2\text{SiO}_3$ .



The solution containing sodium aluminate and sodium silicate is seeded with freshly precipitated aluminium hydroxide. Aluminium hydroxide precipitates leaving behind sodium silicate in solution. This is filtered. Heating aluminium hydroxide at 1473 K yields pure alumina.

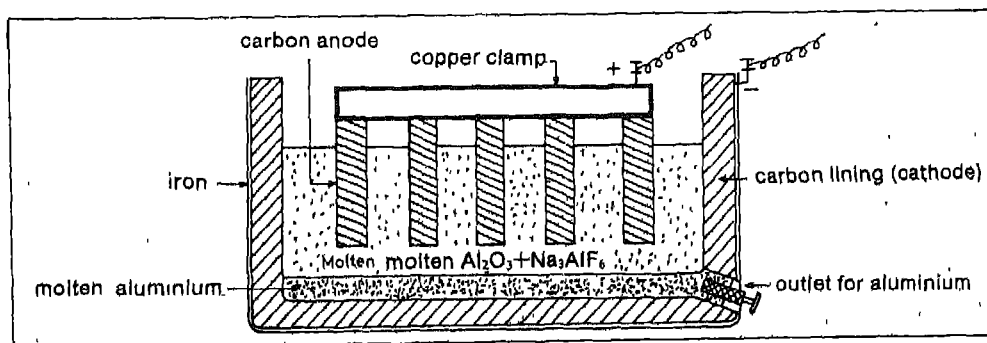
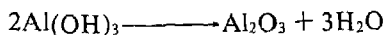
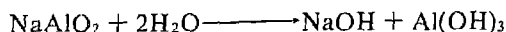
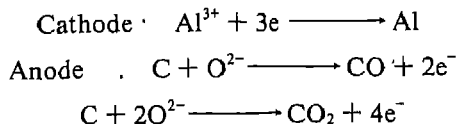


Fig. 14.4 Electrolytic Cell for production of aluminium

(ii) Alumina is dissolved in a fused mixture of cryolite ( $\text{Na}_3\text{AlF}_6$ ) with a little fluorspar ( $\text{CaF}_2$ ), which lowers the temperature of the melt and electrolysed at about 1173 K. The electrolytic cell used for the production of aluminium is given in Figure 14.4

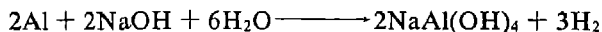


The oxygen evolved at the anode burns the carbon anode producing carbon dioxide, and carbon monoxide. Because of this, the anodes need to be replaced periodically.

### 14.3.2. Properties of Aluminium

Aluminium is a soft, light, silvery white metal with a m.p. 932K. It is quite reactive and readily reacts with oxygen to give  $\text{Al}_2\text{O}_3$ . Because of this, the surface of the metal is always covered with a layer of the oxide.

Aluminium is not attacked by pure water. In saline water, it is easily corroded. Aluminium dissolves in alkali forming hydrogen and the colourless aluminate ion.



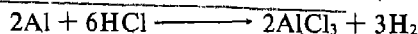
Addition of a small amount of alkali to an aluminium salt solution precipitates aluminium hydroxide. On the addition of more alkali, the hydroxide dissolves to form the aluminate ion.

### 14.3.3 Uses

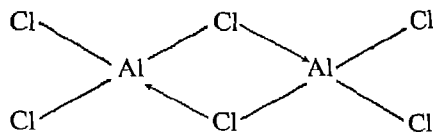
Aluminium is a soft metal with a density of  $2.7 \text{ g cm}^{-3}$ . Aluminium can be easily extruded through dies to form complicated shapes. It is used for making the angles used in windows. It is a good conductor of electricity. Though it is not as good a conductor as copper, thicker cables of aluminium are used for transmission of electricity. Aluminium forms many useful alloys, e.g. manganalium (Al and Mg), duralumin (Al, Cu, Mg and Mn). In view of their low density, aluminium alloys are used in aircraft and other transportation vehicles. In the form of finely divided flakes, aluminium is used as a paint pigment. Aluminium foil is used as a wrapping material. Aluminium is used to produce metals such as chromium and manganese from their ores (aluminothermite process) (Unit 2). Aluminium utensils are extensively used for household purposes.

### 14.3.4 Some Compounds of Aluminium

Aluminium forms many compounds. Among these the halides and sulphates are important. If aluminium is reacted with concentrated or dilute hydrochloric acid, aluminium chloride ( $\text{AlCl}_3$ ) and hydrogen are formed.



Aluminium chloride exists as dimer,  $\text{Al}_2\text{Cl}_6$ , in inert organic solvents as well as in the vapour state. The structure of this dimer is represented as follows.



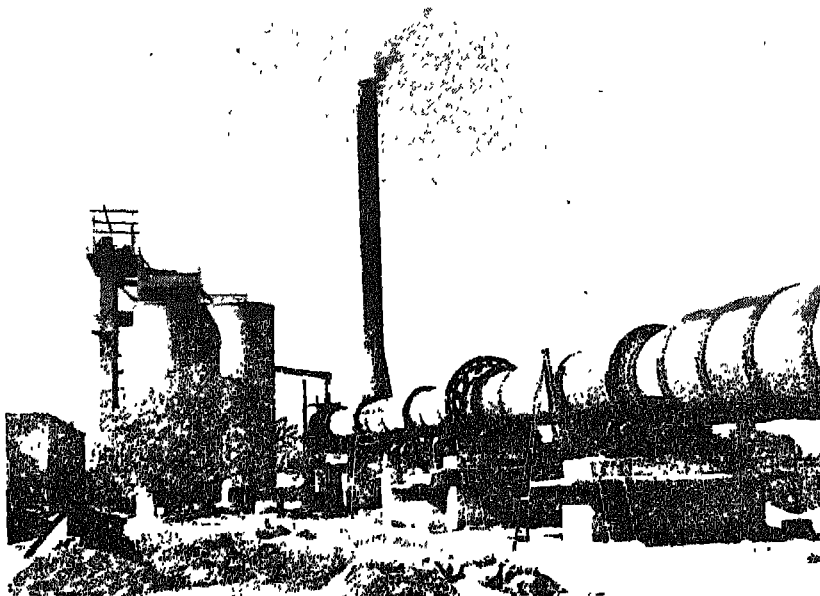
In the above structure, each aluminium atom has achieved an octet configuration by accepting a lone pair of electrons from the chlorine atom of another aluminium chloride molecule. Aluminium sulphate forms double salts with sulphates of other metals. These are called ALUMS. One of the best examples is sodium aluminium sulphate,  $\text{Na}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ . Alums are extensively used for water softening.

## 14 4 CEMENT

We have seen that magnesium, calcium and aluminium form many compounds used in everyday life. Two of the important materials are cement and glass. We have learnt about glass in Unit 13. Here we shall study the nature of cement and its manufacture.

Cement is an important building material. Although the cement industry in India began in 1914, small quantities of the material were being manufactured even at the beginning of the twentieth century using calcium carbonate from sea shells as the basic material. Production of cement is continually on the increase in the country.

Cement is a product obtained by combining a material rich in lime,  $\text{CaO}$  with other materials such as clay which contains silica,  $\text{SiO}_2$ , along with oxides of



**Photo IV** *The kiln where raw materials are baked to cement (a cement factory in Punjab)*

Courtesy: P.I B. New Delhi

aluminium, iron and magnesium. The composition of the metal oxides could be different in different types of cements. The average composition of Portland cement is  $\text{CaO}$ , 50-60%,  $\text{SiO}_2$ , 20-25%,  $\text{Al}_2\text{O}_3$ , 5-10%,  $\text{MgO}$ , 2-3%,  $\text{Fe}_2\text{O}_3$ , 1-2% and  $\text{SO}_3$ , 1-2%. For a good quality cement, the ratio of silica ( $\text{SiO}_2$ ) to alumina ( $\text{Al}_2\text{O}_3$ ) should be between 2.5 and 4.0 and the ratio of lime ( $\text{CaO}$ ) to total oxides of silicon ( $\text{SiO}_2$ ), aluminium ( $\text{Al}_2\text{O}_3$ ) and iron ( $\text{Fe}_2\text{O}_3$ ) should be as close to 2.5 as possible.

The raw materials for the manufacture of cement are limestone and clay. When clay and lime are strongly heated together, they fuse and react to form CEMENT CLINKER. It is a complex mixture of calcium silicate and calcium aluminate. The clinker is mixed with 2-3% by weight of gypsum ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ) to regulate its setting time and is then ground to an exceedingly fine powder.

Lime stone and clay are powdered and mixed	Burnt at 1770-1870 K in Rotary kiln	Calcium silicate $\text{Ca}_3\text{Si}_2\text{O}_7$ , $\text{Ca}_2\text{SiO}_4$ Calcium aluminate $\text{Ca}_3\text{Al}_2\text{O}_6$ , $\text{Ca}_2\text{Al}_2\text{O}_5$ 'cement clinker'	addition of gypsum	Portland cement
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When mixed with water the cement reacts to form a gelatinous mass which sets to a hard mass when three dimensional cross links are formed between  $\text{---Si---O---Si---}$  and  $\text{---Si---O---Al---}$  chains.

There are many materials which possess properties similar to cement. One of them is fly ash, a waste product from the steel industry. This can be added to cement to reduce the cost without affecting the quality. Rice husk which has high silica content has been employed to make cement.

#### 14.5 BIOLOGICAL ROLE OF SODIUM, POTASSIUM, MAGNESIUM AND CALCIUM

Sodium and potassium are the most common cations in biological fluids. Interestingly, many cells tend to accumulate  $\text{K}^+$  ions at the expense of  $\text{Na}^+$  ions. Typically, in red blood cells, the ratio of potassium to sodium is 7:1 in mammals such as human beings, rabbits, rats and horses. This ratio is 1:1.5 in cats and dogs. In order to establish this concentration gradient in the cell, work has to be done. Biologists propose different mechanisms such as the SODIUM PUMP and the POTASSIUM PUMP. The most remarkable feature of these cation gradients is the development and functional features of nerve cells. In the resting state, a nerve cell exhibits a potential corresponding to the potassium concentration across the membrane. During activation of nerve cells, a chemical (e.g., acetyl choline) is released near its end plate and the membrane potential is discharged. This discharge is transmitted through the length of the nerve cell by an electric pulse. This action illustrates the importance of sodium and potassium cations.

Magnesium and calcium play an important role in biological reactions. The main pigment for the absorption of light in plants is chlorophyll which contains magnesium. Imagine what life would be without photosynthesis!

Calcium occurs generally in animal bones as phosphate. Very little is known

about the changes in bone structure as one grows old. Calcium ions also play an important role in muscle contraction. These functions are related to energy storage in biological systems in the form of pyrophosphate linkages. These linkages are formed through a catalytic role by Mg or Ca ions. The pyrophosphate undergoes hydrolysis with the release of energy. This process is controlled by calcium ions.

There are many enzyme reactions that are controlled by alkali and alkaline earth cations. Chemists have not yet fully understood the role of alkali and alkaline earth cations in biology although their importance has been recognised.

### HOW IMPORTANT ARE SILICATES?

Silicate rocks and minerals play a very important role in providing a strong solid structure to the earth. Silicate rocks, which make up the majority of the rocks on earth, vary greatly in their compositions. Some contain discrete silicate ions, like orthosilicate ions,  $\text{SiO}_4^{4-}$  and other pyrosilicate ions,  $\text{Si}_2\text{O}_7^{6-}$ , but most silicate rocks contain hundreds of thousands or millions of atoms connected in chains (Fig 14.5), sheets or in three dimensional network (called polymeric silicates). Polymeric silicate anions are found in *micas* and *clays*. Since these rocks are electrically neutral, they must also contain a sufficient number of cations (such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ) to equalise all the negative charges carried by the oxygen atoms. The combination of different forms of silicate ions, and different cations, produces many kinds of

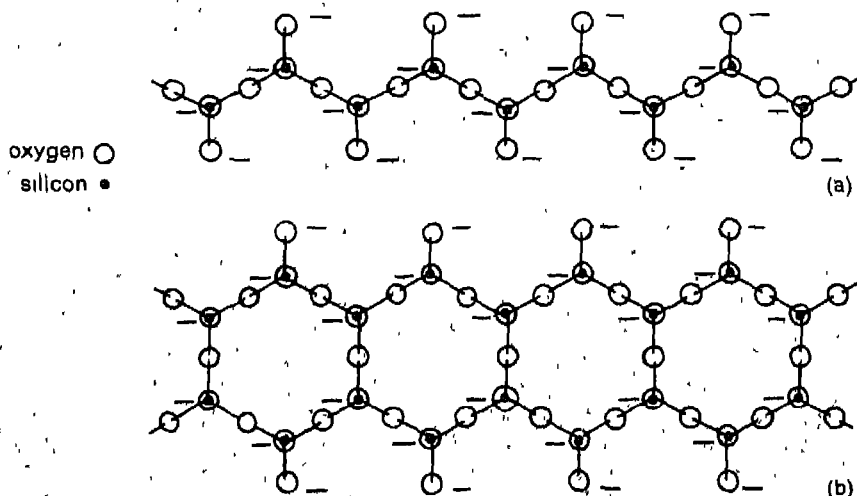


Fig. 14.5 Chain silicates: (a) Sharing of two oxygens by each  $\text{SiO}_4^{4-}$  tetrahedron resulting in a simple chain, (b) Joining of two simple chains by shared oxygen, resulting in a double chain.

silicate rocks and minerals. The situation is even more complicated by the fact that nature is seldom interested in preparing pure compounds, so that many individual rocks are mixtures.

In a silicate structure, some of the  $\text{Si}^{4+}$  ions can be replaced by  $\text{Al}^{3+}$  ions and the network must then carry an overall negative charge which is balanced by the incorporation of cations such as  $\text{Na}^+$  and  $\text{Ca}^{2+}$  into the structure. Compounds of this type are called aluminosilicates; one example is *analcite*, which is a *zeolite* (empirical formula,  $\text{Na}^+(\text{AlSi}_2\text{O}_6)^- \cdot \text{H}_2\text{O}$ ). Both natural and synthetic zeolites have a very open structure which allows ion-exchange to take place and they are used in the treatment of *hard water*. When anhydrous, they can function as 'molecular sieves'. Only recently a zeolite has been found which can adsorb straight chain alkanes but not branched chain or aromatic substances, thus effecting their separation.

As seen earlier, glass is also a mixture of sodium and calcium silicates. In manufacture of cement, when clay and limestone are strongly heated together, they fuse and react to form *cement clinker* which is a complex mixture of calcium silicates and aluminium silicates.

## EXERCISES

- 14.1 What are the common physical and chemical features of alkali metals?
- 14.2 List some important ores of sodium and potassium.
- 14.3 Explain the following:
  - (i) Alkali and alkaline earth metals cannot be obtained by chemical reduction methods.
  - (ii) Ionisation energies of alkali metals decrease as the atomic number increases.
  - (iii) Group 2 metals (Mg and Ca) are harder and denser than group 1 metals (Na and K).
  - (iv) It is necessary to pretreat the bauxite ore before electrolysis to obtain aluminium.
- 14.4 Discuss the various reactions in the Solvay process.
- 14.5 With the help of a diagram, show the reactions at the cathode and the anode in the manufacture of sodium hydroxide by the Castner-Kellner process?
- 14.6 How does magnesium occur in nature? How is magnesium metal obtained by the electrolysis method?



14.7 Name a few important uses of the following compounds.

- (i) Sodium bicarbonate
- (ii) Epsom salt
- (iii) Quick lime/ slaked lime
- (iv) Sodium hydroxide.

14.8 Bones contain calcium ions. What do you think would be the anions associated with it?

14.9 Describe the electrolysis process to obtain aluminium metal from bauxite.

14.10 The hydroxides and carbonates of sodium and potassium are easily soluble in water while the corresponding salts of magnesium and calcium are sparingly soluble in water. Explain.

14.11 What chemical test would you perform to detect sodium, magnesium, calcium and aluminium ions in a given solution?

14.12 What is the effect of heat on the following compounds? (Write equations for the reactions).

- (i) Calcium carbonate
- (ii) Magnesium chloride hexahydrate
- (iii) Gypsum
- (iv) Magnesium sulphate heptahydrate.

14.13 Name a few alloys of aluminium.

14.14 Explain the significance of sodium and potassium in biological fluids.

14.15 Explain the following:

- (i) Aluminium is used for electrical cables though it is relatively less conducting than copper.
- (ii) A piece of burning magnesium ribbon continues to burn in sulphur dioxide.
- (iii) Aluminium dissolves both in acidic and basic solutions.
- (iv) It is necessary to add gypsum in the final stages of preparation of cement.

## CHEMISTRY OF HEAVIER METALS

[illegible]

- \* the general properties of a few heavier metals such as tin, lead, iron, zinc, mercury, copper, silver and gold;
- \* the steps involved in the extraction of these metals from their ores;
- \* a few commonly used alloys of these heavier metals,
- \* the preparation, properties and uses of oxides, sulphides and halides of these metals;
- \* the chemical principles of photography.

PRODUCTION OF METALS and their uses either in the pure form or when mixed with one another to form alloys have been known since ancient times. Some of the common metals that we encounter are tin, lead, iron, cobalt, nickel, copper, silver, gold, zinc and mercury. These metals have played an important role in the bronze and the iron age as well as in the industrial revolution. Even today, in the atomic age or the space age, they continue to play a leading role.

We studied in Unit 2 the various steps involved in the metallurgical operations for the extraction of metals. In this Unit, we shall study the extraction of some common heavier metals from their ores. Alloys of some of these metals find wide applications. The preparation, properties and uses of some of the common compounds of these metals will also be discussed in this Unit.

Iron, zinc, mercury, copper, silver and gold are transition elements (d-block elements). Tin and lead are neighbours of transition elements and belong to group 14 in the periodic table. The change-over from non-metallic to metallic nature with increasing atomic number can be seen clearly in the elements of group 14, and we study them, together.

### 15.1 IRON (Fe)

Iron is the second most abundant metal occurring in the earth's crust. It is an element of the first transition series. Some of its general properties are given in table 15.1

TABLE 15.1

Some General Properties of Iron

Element	Atomic number	Electronic configuration	Atomic radius (pm)	Ionic radius (pm)		<i>m.p.</i> (K)	<i>b.p.</i> (K)	Density $\text{g cm}^{-3}$	Oxidation states
				$M^{2+}$	$M^{3+}$				
Iron (Fe)	26	$[\text{Ar}] 3d^6 4s^2$	126	76	64	1809	3273	7.86	+2, +3

#### 15.1.1 Occurrence and Extraction

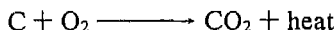
The chief ores of iron are the oxides in different forms such as HAEMATITE,  $\text{Fe}_2\text{O}_3$ , MAGNETITE,  $\text{Fe}_3\text{O}_4$ , LIMONITE, or hydrated ferric oxide,  $(\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O})$ , SIDERITE,  $\text{FeCO}_3$  and IRON PYRITES,  $\text{FeS}_2$ .

In India, iron ores are found chiefly in the states of Bihar, Orissa, West Bengal and Karnataka. Iron and steel producing factories in India are located at Asansol, Jamshedpur, Bhilai, Durgapur, Rourkela, Bhadravati and Bokaro.

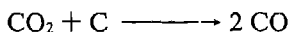
The three forms of iron used widely are cast iron, wrought iron and steel. They differ in properties because of their carbon and phosphorus content.

Extraction of iron from its ores consists of two processes, (i) Smelting to obtain the crude metal, and (ii) refining of the crude metal. Smelting is carried out in a

blast furnace (a steel vessel lined with fire bricks). Iron ore (generally haematite) is calcined to remove volatile impurities, like sulphur and arsenic. The calcined ore along with limestone and coke are lifted to the top of the furnace and released when needed. Preheated air at a temperature of about 873 K is passed into the furnace through a number of nozzles. Near the bottom, preheated air comes in contact with the falling coke and combustion of coke takes place



The reaction is highly exothermic. This  $\text{CO}_2$  goes upwards and comes into contact with layers of coke and gets reduced to  $\text{CO}$ .



CO acts as a reducing agent and reduces iron oxide to iron.

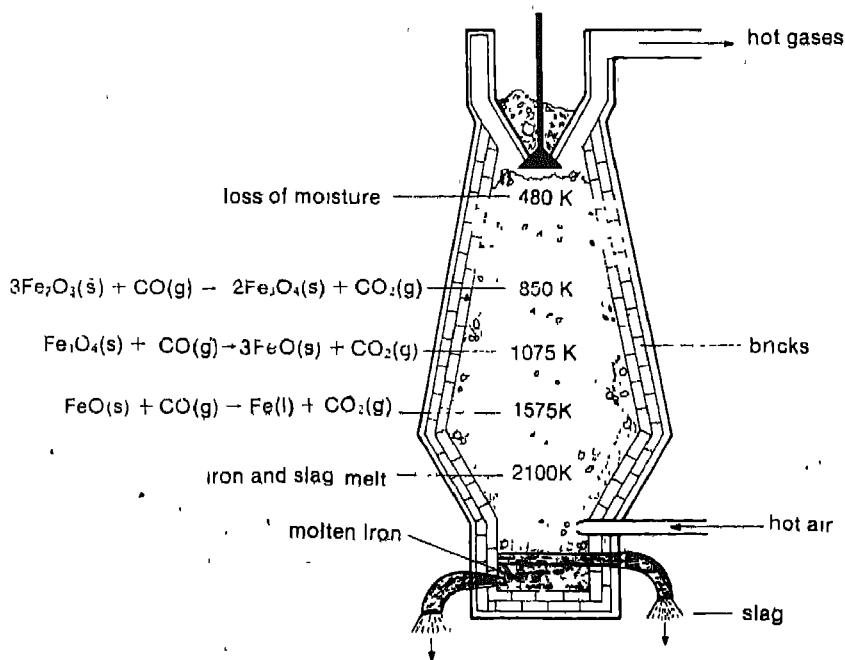
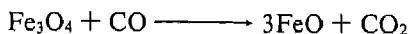
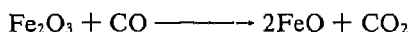
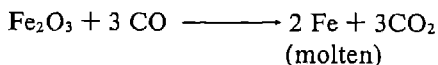
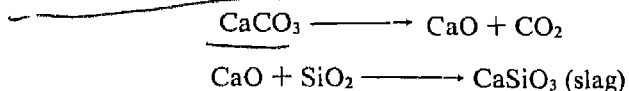


Fig 15.1 Reactions in the blast furnace for the manufacture of iron

Molten iron thus formed is collected at the bottom from where it is tapped off.

Limestone which acts as a flux decomposes at about 1073 K. The quicklime reacts with sandy impurities ( $\text{SiO}_2$ ) to form a slag of calcium-silicate.



The molten slag is less dense than iron and floats on the top. When both molten iron and slag are drawn off, coke and limestone are added. The gases leaving the furnace contain CO and are used to heat the incoming air-blast. The whole blast furnace process is continuous.

The molten iron tapped off from the furnace is solidified into blocks known as

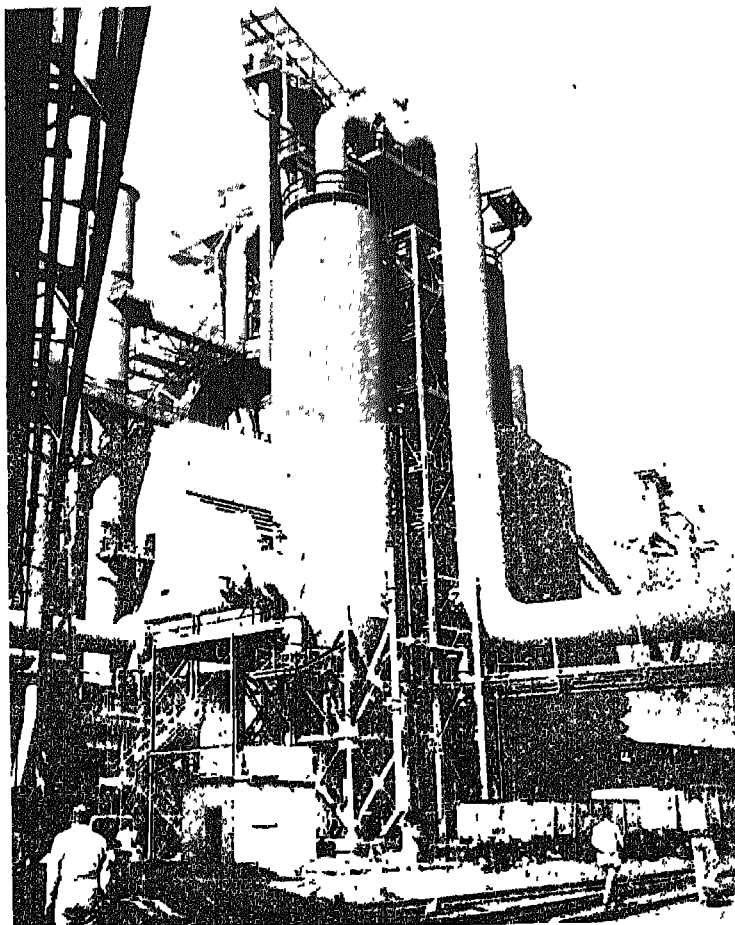
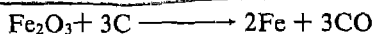


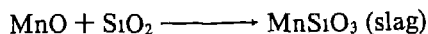
Photo V General view of Durgapur steel plant

'pigs' This form of iron is called 'pig iron' or cast iron. It contains about 3-5% carbon and varying amounts of Mn, Si, S, and P. The presence of these impurities makes the iron hard and brittle. Cast iron cannot be forged or welded by hammering. When molten cast iron solidifies, it expands slightly. It, therefore, finds extensive applications in casting various shaped articles, such as toys, radiators, stools, pipes and agricultural implements.

Cast iron is either converted to wrought iron or steel. Wrought iron which is a comparatively pure form of iron is obtained by refining cast iron. The cast iron is heated with haematite ( $\text{Fe}_2\text{O}_3$ ) so that the impurities are oxidised.



Carbon monoxide escapes while  $\text{MnO}$ , present as an impurity, combines with  $\text{SiO}_2$  to form manganous silicate ( $\text{MnSiO}_3$ ) a slag.



Wrought iron thus formed contains about 0.2-0.5% carbon and traces of P and Si in the form of slag. Wrought iron is ductile, soft and malleable. The presence of slag in the iron makes it tough and resistant towards rusting and corrosion. It is used to make magnets in electric cranes and dynamos. It is also used to make articles such as chains, anchors, bolts, nails and railway carriage couplings.

Iron by itself is not very useful, but the addition of metals and carbon converts it into steel. The various steels have a carbon content varying from 0.1 to 1.5%. By increasing the carbon content in steel, its ductility decreases and its tensile strength increases.

There are three methods commonly used for the production of steel on a large scale. They are: (i) the Bessemer Process, (ii) the Open Hearth Process, and (iii) the Electric Furnace Process. Molten pig iron is poured into the Bessemer converter which is made of steel and lined with refractory material (silica bricks). The initial temperature rises rapidly to approximately 1873 K. Impurities such as Mn, Si, and C burn off. When all the carbon is completely removed, the requisite amount of carbon is added to convert iron into steel.

If cast iron contains appreciable levels of phosphorus, the converter is lined with lime ( $\text{CaO}$ ) and magnesia ( $\text{MgO}$ ) instead of  $\text{SiO}_2$ . Some lime is added to the molten cast iron. The phosphorus present as an impurity is oxidised to  $\text{P}_2\text{O}_5$  which forms a slag,  $\text{Ca}_3(\text{PO}_4)_2$ .

A steel of more exact composition is obtained by the open hearth process. In this process, a mixture of cast iron, scrap iron, iron ore (haematite) and lime is melted in an open hearth furnace. The hearth is lined with  $\text{SiO}_2$  or calcined dolomite ( $\text{MgO}$ ,  $\text{CaO}$ ) depending upon the nature of the impurities present in the cast iron. Heating to about 1873 K is done by burning fuel gas and air. The slag formed over the surface protects the steel from oxidation. The process is much slower but a better quality of steel is formed.

In recent years a combination of the Bessemer and the open hearth processes has been employed. The electric furnace method differs from the open hearth process

primarily in the method of heating

*Properties of steel:* The hardness of steel depends on its carbon content and heat treatment. Hard steel can be further hardened by heating it to red hot (1123 K) and cooling it by plunging it into cold water. This process is called QUENCHING. It makes the steel hard and brittle. If the quenched steel is reheated to a temperature between 503K and 573K and allowed to cool slowly, it retains its hardness but the brittleness disappears. This process is known as TEMPERING. If steel is heated to a temperature well below red heat and is then cooled slowly, the process is called ANNEALING. Annealed steel is soft.

Steels have carbon contents varying from 0.1 to 1.5%. Other elements are added during the manufacture of steel to impart certain properties. Mild steel contains carbon between 0.1 and 0.4%. Hard steel contains between 0.5 to 1.5% carbon. Hard steel can be further hardened by heat treatment and is used for tools. A few examples of alloy steels are given in Table 15.2

TABLE 15.2  
Some Alloy Steels

Name of alloy	Percentage composition	Properties	Uses
Stainless steel	Fe — 73 ✓ Cr — 18 ✓ Ni — 8 ✓ and carbon ✓	Resists corrosion	Ornamental pieces, cutlery
Manganesec steel	Fe — 86 Mn — 13 and carbon	Very hard, resistant to wear	Rock drills, safes
Tungsten steel	Fe — 94 W — 5 and carbon	Hard	High speed cutting tools
Invar	Fe — 64 Ni — 36	Small coefficient of expansion	Watches, meter scales, pendulum rods
Nickel steel	Fe — 98-96 Ni — 2-4	Resistant to corrosion, hard and elastic	Wire cables, gears, drive shafts
Pernitalloy	Fe — 21 Ni — 78 and carbon	Strongly magnetised by electric current, loses magnetism when current is cut off	Electromagnets, ocean cables

### 15.1.2 Compounds of Iron

Iron forms many compounds in both the oxidation states, two and three.

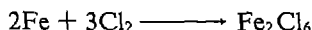
#### *Oxides of Iron*

Iron forms three oxides—FeO, Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>. We encountered all the three oxides in the metallurgy of iron. Iron (II) oxide, FeO and Iron (III) oxide, Fe<sub>2</sub>O<sub>3</sub> form iron

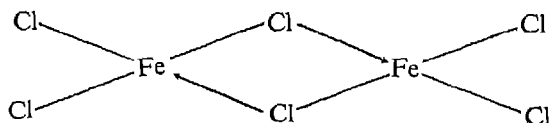
(II) and iron (III) salts on treatment with acids.  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  occur in nature as haematite and magnetite, respectively. These are the two major sources of iron and steel.

### *Halides of Iron*

Anhydrous ferric chloride,  $\text{FeCl}_3$ , is obtained by heating iron filings in a stream of chlorine gas. The product collects in the form of deep red-black, flaky crystals.

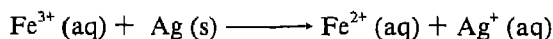
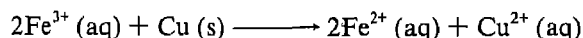


It is a covalent compound. It dissociates on heating above 973 K first into  $\text{FeCl}_3$  and then into  $\text{FeCl}_2$  and  $\text{Cl}_2$ . The structure of  $\text{Fe}_2\text{Cl}_6$  is as follows:



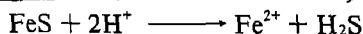
It is soluble in water, alcohol and ether and forms hydrates. The most common hydrate of iron,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , is yellow in colour. The aqueous solution is strongly acidic due to hydrolysis.

$\text{Fe}_2\text{Cl}_6$  is used in medicine as an astringent and as an antiseptic (in the form of tincture). On hydrolysis, it gives  $\text{Fe}(\text{OH})_3$ , which is an important mordant in dyeing. Block-makers use a concentrated solution of  $\text{FeCl}_3$  for etching metals like copper and silver. This is due to the oxidising action of  $\text{Fe}^{3+}$ .



### *Sulphides of Iron*

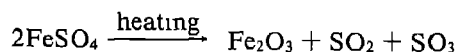
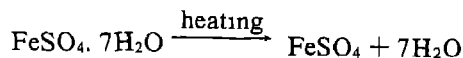
Iron(II) sulphide,  $\text{FeS}$ , is obtained by heating iron filings with sulphur. It is used to prepare  $\text{H}_2\text{S}$  gas in the laboratory by the action of dilute acid.



### *Sulphates of Iron*

One of the commercially important sulphates of iron,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , is called Green Vitriol because of its green colour. It is prepared by the action of dilute  $\text{H}_2\text{SO}_4$  on iron. This salt should be made in a reducing atmosphere in order to prevent the oxidation of  $\text{Fe}^{2+}$  into  $\text{Fe}^{3+}$ .

On heating, green  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  gives a white anhydrous salt. On strong heating, it forms  $\text{Fe}_2\text{O}_3$ ,  $\text{SO}_2$  and  $\text{SO}_3$ .





Iron (II) sulphate and other iron (II) salts combine with nitric oxide, NO, and form a brown coloured double compound,  $\text{Fe(NO)SO}_4$ . This is the basis of the 'brown ring' test for ionic nitrates.

Iron (II) sulphate is an efficient reducing agent. It reduces potassium permanganate and potassium dichromate

Iron (II) sulphate is one of the cheapest industrial chemicals and is used to make iron (III) oxide. Iron (II) sulphate forms double salts with sulphates of monovalent cations. Iron (II) ammonium sulphate,  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  commonly known as Mohr salt is the most important double salt. It is prepared by crystallising a solution containing equivalent amounts of iron (II) sulphate and ammonium sulphate. It is commonly used to prepare standard solutions of iron (II) by direct weighing (primary volumetric standard) and also to standardise  $\text{KMnO}_4$  solution. Iron (III) ammonium sulphate,  $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$  known as ferric alum is commercially important.

## 15.2 COPPER, SILVER AND GOLD (Cu, Ag and Au)

These elements have been known to mankind since ancient times and have been used for decorative purposes from time immemorial. Some general properties of these elements are given in Table 15.3.

TABLE 15.3

Some General Properties of Copper, Silver and Gold

Element	Atomic number	Electronic configuration	Atomic radius (pm)	Ionic radius (pm) (M <sup>+</sup> )	m.p. (K)	b.p. (K)	Density g cm <sup>-3</sup>	Oxidation states
Copper (Cu)	29	$[\text{Ar}]3d^{10}4s^1$	128	96	1356	2868	8.92	+1, +2
Silver (Ag)	47	$[\text{Kr}]4d^{10}5s^1$	144	126	1233	2485	10.5	+1
Gold (Au)	79	$[\text{Xe}]5d^{10}6s^1$	144	137	1333	3239	19.3	+1, +3

16.15.1  $[\text{Xe}] = 67$   
 The atoms of Cu, Ag and Au have one electron in the outermost shell like the atoms of alkali metals. But the atoms of alkali metals have eight electrons in the penultimate shell, whereas the atoms of Cu, Ag and Au have eighteen electrons. The properties of Cu, Ag and Au are quite different from those of alkali metals.

### 15.2.1 Occurrence and Extraction

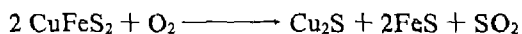
#### Copper

Copper occurs as native copper as well as in combined state. Native copper is found

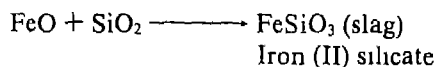
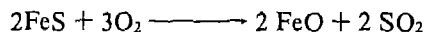
in large quantities in Michigan (U.S.A). The principle ores of copper are, COPPER GLANCE,  $\text{Cu}_2\text{S}$ , COPPER PYRITES,  $\text{CuFeS}_2$ , CUPRITE,  $\text{Cu}_2\text{O}$  and MALACHITE,  $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$ .

Commercially viable deposits of copper are found in Karnataka and Rajasthan. In Rajasthan, the Khetri copper belt is an important source of copper. It is also found at various places along the outer Himalayas. Khetri, Garhwa and Sikkim are the places in the Himalayan belt. In Singhbhum district (Bihar) there is a long copper bearing belt. Malachite and cuprite ores are found in the Mosaboni area.

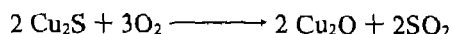
Copper is extracted mainly from copper pyrites. The powdered ore, after concentration by the floatation process, is roasted in a limited supply of air in a reverberatory furnace to convert iron into iron (II) oxide. Arsenic and antimony present as impurities are removed as volatile oxides.



The roasted ore is then mixed with sand and heated strongly in a blast furnace. Most of the iron sulphide is converted into iron oxide. It combines with silica and is removed as slag.



Copper is then recovered from the molten matte obtained from the furnace. The molten matte is transferred to a Bessemer converter and a blast of air is blown through the molten matte. This operation reduces Copper (I) sulphide to copper.



The molten copper thus obtained is about 99% pure and is used for many purposes.

Impure copper is further refined electrolytically to obtain 99.95-99.99% pure copper by using a solution of copper(II) sulphate as the electrolyte. An anode sludge (anode mud) containing silver and gold settles down. (Why does the anode sludge contain silver and gold?)

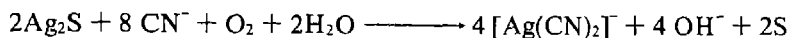
### Silver

Silver occurs as native silver as well as in the combined state. Its principal ores are ARGENTITE (silver glance),  $\text{Ag}_2\text{S}$ , HORN SILVER  $\text{AgCl}$  and PYRARGYRITE (ruby silver),  $\text{Ag}_3\text{S} \cdot \text{Sb}_2\text{S}_3$ .

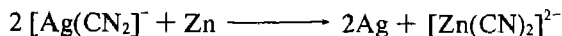
The silver content in these ores is small (about 1%). Silver is also present in small quantities in lead, copper and zinc ores.

India does not have silver ores. Silver is mostly obtained as a by-product in the mining of gold and lead. Silver is also obtained to a small extent from the gold ores in the Kolar fields in Karnataka and in the Anantpur mines.

For the extraction of silver from its ores, the powdered ore is treated with a dilute solution of sodium cyanide (0.5%) for several hours. This mixture is continuously agitated by a current of air. Metallic silver or silver from the ore goes to the solution in the form of a complex ion,  $[\text{Ag}(\text{CN})_2]^-$



The soluble silver complex is removed and treated with zinc dust. Silver precipitates out



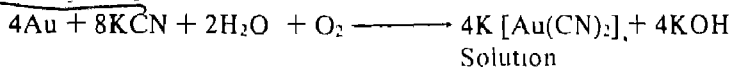
Pure silver is obtained by the electrolysis of a solution of silver nitrate and nitric acid. The impure silver acts as the anode and a pure strip of silver serves as the cathode. A significant amount of silver is also obtained during the extraction of Pb from its ores and from the ANODE MUD obtained in the electrolytic refining of copper.

### Gold

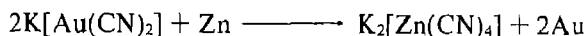
Gold is usually found as NATIVE GOLD either mixed with quartz, in ancient rocks or in alluvial soils. It is present in the alluvial sands of rivers that pass over auriferous rocks. It also occurs in the form of sulphide, telluride, and arsenosulphide. Nearly half of the total world production of gold is from the mines in South Africa.

India occupies the eighth position amongst the gold-producing countries. Its contribution is about two per cent of the world production. The Kolar mines in Karnataka produce about 99.97 per cent of our gold output. Alluvial gold is widely distributed in Chhota Nagpur but the gold washing is mostly done in Singhbhum and Manubhum districts in the valleys of the Suvernakha river. Extraction of gold involves dissolving the gold, filtering, and then precipitating the gold. The suspension obtained after dissolving the gold is filtered through a fine filter. The gold particles adhere to the copper plates to which the gold particles adhere. The gold amalgam thus formed is scraped and distilled in iron retorts. Mercury distills over leaving behind the gold.

Gold ore (sulphide) is roasted to remove the sulphur. The roasted ore is then treated with a solution of KCN. KCN forms an orange-red complex.



The metal is then precipitated by adding zinc shavings



This process is called Mac Arthur-Forest Cyanide Process. Sodium and potassium cyanides are extremely poisonous and must be handled with utmost care.

Gold so obtained is impure and is contaminated with metals like Ag and Cu (Removal of silver and copper from gold is done by parting). It is done by boiling impure gold with concentrated  $H_2SO_4$ . Silver and copper dissolve in this acid while gold remains unaffected. Parting can also be carried out by boiling an impure sample with nitric acid.

Impure gold is also refined electrolytically by using an acidified solution of gold (III) chloride,  $AuCl_3$ , as the electrolyte.

### 15.2.2 Properties and Uses of Cu, Ag and Au

Copper is red-brown with a high lustre, but the surface is often dulled by oxide formation. Silver is a white lustrous metal whereas gold is a soft, heavy and yellow metal with a high lustre. Gold and silver are known as 'noble' metals as they are unattacked by atmospheric oxygen. However, silver becomes tarnished when exposed to air containing traces of hydrogen sulphide. These metals are malleable and ductile. They are good conductors of heat and electricity.

#### Uses

Copper forms a large number of alloys with other metals, such as tin, zinc, nickel, aluminium, etc. Some of the most important alloys of copper are given in Table 15.4.

TABLE 15.4

Important Alloys of Copper

Alloy	Percentage composition	Uses
Bronze	Cu-80, Zn-10, Sn-10	For making statues, coins, cooking utensils
Brass	Cu-80, Zn-20	For making utensils, parts of machinery, wires
Gun metal	Cu-90, Sn-10 ✓	For making gun barrels
Constantan	Cu-60, Ni-40 ✓	For electrical apparatus

Copper is extensively used for making electric cables and other electric appliances. It is used in making utensils, containers, kettles, evaporating pans, coins and calorimeters as copper is not attacked by water or air. Copper is used for electroplating and electrotyping. It is also used for making a large number of alloys. Copper is alloyed with gold and silver for making ornaments and coins.

Silver being very soft is alloyed with copper. Silver alloy used for making ornaments contains about 80% Ag and 20% Cu. The composition of a silver alloy is expressed as its 'fineness', i.e., the amount of Ag in 1000 parts of the alloy. '925 fine silver' means an alloy of 92.5% silver and 7.5% copper.

Pure gold is soft and is generally hardened by adding silver or copper to it for

the purpose of making jewellery The weight of gold in jewellery is expressed in carats. It signifies the number of parts by weight of gold in 24 parts by weight of the alloy. Pure gold is 24 carats. Gold '18 carat' means that it contains 18 parts by weight of pure gold. Most jewellery is made out of 22 carat gold. Gold is also used for plating articles made of copper alloys.

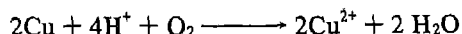
### *Chemical Properties*

The reactivity of these three metals decreases with increasing atomic number (i.e., in the order Cu, Ag, Au). The metals are not attacked by water or steam at ordinary temperatures.

Only copper is attacked by oxygen, first forming copper(I) oxide,  $\text{Cu}_2\text{O}$  (red) and then copper(II) oxide,  $\text{CuO}$  (black). In the presence of atmospheric  $\text{CO}_2$  and moisture, copper is covered with a green layer of the basic carbonate,  $\text{CuCO}_3$ . This layer protects the metal from further action. Silver and gold are resistant to attack by air and moisture, although the presence of  $\text{H}_2\text{S}$  in air results in the formation of a black stain of silver sulphide ( $\text{Ag}_2\text{S}$ ).

None of the metals displaces hydrogen from acids. They are not attacked by dilute non-oxidising acids such as dilute  $\text{HCl}$  and dilute  $\text{H}_2\text{SO}_4$  in the absence of an oxidising agent.

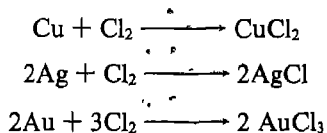
Copper dissolves more readily in acids when oxygen is bubbled through them, forming copper (II) ions



Copper and silver react with concentrated  $\text{H}_2\text{SO}_4$  to form  $\text{Cu}^{2+}$  and  $\text{SO}_2$ . Copper and silver are attacked by dilute and concentrated  $\text{HNO}_3$  to form  $\text{NO}$  and  $\text{NO}_2$  respectively (Unit 12).

Gold is very inert and does not react with oxygen, water or acids. It is, however, attacked by a mixture of concentrated  $\text{HCl}$  (3 parts) and concentrated  $\text{HNO}_3$  (1 part), known as AQUA REGIA

Chlorine attacks the metals to give their chlorides

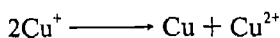


### 15.2.3 Compounds of Cu, Ag and Au

All the three metals exhibit an oxidation state of +1. In this state, their compounds are largely ionic. The principal oxidation states of Cu, Ag and Au are +2, +1 and +3 respectively.

Cu(I) gets oxidised easily to the Cu(II) state which is more stable. Thus, copper mostly forms bivalent compounds.

The  $\text{Cu}^+$  ion is colourless. All copper(I) salts decompose in water. Half the copper(I) is transformed to copper metal and the other half goes to copper(II). This reaction is called DISPROPORTIONATION REACTION



In aqueous solution, copper(II) salts are blue.

*Oxide.* Copper (II) oxide,  $\text{CuO}$ , is obtained as a black solid by heating either copper (II) carbonate (basic carbonate) or copper (II) nitrate. On heating to a higher temperature (1073K), it decomposes into copper(I) oxide,  $\text{Cu}_2\text{O}$ , and oxygen.

Copper (II) oxide reacts with dilute mineral acids and forms copper (II) salts on warming. It is also reduced to copper on heating in a stream of  $\text{H}_2$ .

Silver oxide,  $\text{Ag}_2\text{O}$  is thermally unstable and decomposes into silver and oxygen on slow heating.

### Sulphides

Copper (II) sulphide,  $\text{CuS}$ , and silver(I) sulphide,  $\text{Ag}_2\text{S}$ , precipitate as black solids when  $\text{H}_2\text{S}$  is passed through aqueous salt solutions in the presence of acid. Gold(I) sulphide is the most stable sulphide of gold and is formed by passing  $\text{H}_2\text{S}$  gas through an acidified solution of potassium aurocyanide,  $\text{K}[\text{Au}(\text{CN})_4]$ . It is a dark brown solid, insoluble in water and not attacked by mineral acids.

### Halides

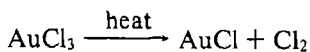
Copper (II) chloride,  $\text{CuCl}_2$ , is prepared by passing chlorine over heated copper. Anhydrous  $\text{CuCl}_2$  is a dark brown solid. It is soluble in water and forms a number of hydrates. Concentrated aqueous solution of  $\text{CuCl}_2$  is dark brown which changes on dilution to green and then to blue.

Copper (I) chloride,  $\text{CuCl}$ , is a white solid insoluble in water. It can be obtained by boiling a solution of  $\text{CuCl}_2$ , excess of copper turnings and concentrated  $\text{HCl}$ . On pouring the solution into air-free distilled water, copper(I) chloride precipitates out as a white solid. It is rapidly washed, dried and sealed in the absence of air, as it combines with air and moisture and forms  $\text{CuCl}_2$ .

Copper (I) chloride is used in combination with  $\text{NH}_4\text{Cl}$  as a catalyst in the production of synthetic rubber.

Silver chloride is obtained as a white precipitate when a solution containing chloride ions is mixed with a solution containing  $\text{Ag}^+$  ions. It is insoluble in water but soluble in ammonia, sodium thiosulphate and potassium cyanide. Similarly, on mixing a solution of  $\text{Ag}^+$  with a solution containing  $\text{Br}^-$  or  $\text{I}^-$ ,  $\text{AgBr}$  or  $\text{AgI}$  precipitates out. Silver bromide is partially soluble whereas  $\text{AgI}$  is completely insoluble in ammonia solution. Thus, the solubility in ammonia solution decreases in the order  $\text{AgCl} > \text{AgBr} > \text{AgI}$ . All the three halides are photosensitive.

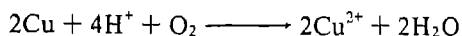
Gold (III) chloride,  $\text{AuCl}_3$ , known as auric chloride forms red crystals which are soluble in water. It is obtained by passing dry chlorine over gold leaves or finely divided gold powder at about 573 K. On heating, it decomposes to gold (I) chloride,  $\text{AuCl}$  and  $\text{Cl}_2$ .



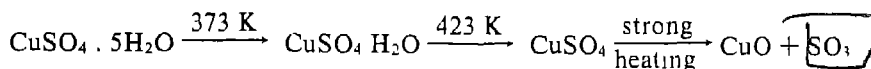
### Copper Sulphate

Copper (II) sulphate, commonly known as BLUE VITRIOL is prepared by dissolving

copper (II) oxide, or copper (II) carbonate in dilute sulphuric acid. The solution is concentrated by evaporation. Blue crystals of copper (II) pentahydrate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , separate out on cooling. On a large scale, copper (II) sulphate is obtained by forcing air through a hot mixture of copper and dilute  $\text{H}_2\text{SO}_4$ .



On heating,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  loses water molecules as follows



Copper sulphate is extensively used in electroplating, electric batteries and as a mordant in dyeing. A mixture of copper sulphate and lime, under the name of BORDEAUX MIXTURE is used as a fungicide in agriculture. It is also used in textile dyeing and as a timber preservative.

#### 15.2.4 Photography

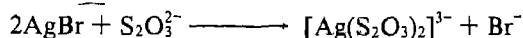
The process of producing pictures by using light images is called 'photography'. It is based on the fact that silver halides, especially  $\text{AgBr}$ , are highly photosensitive. The various steps involved in obtaining a photograph are given below.

(i) The photographic film is made from celluloid. It is uniformly coated with a colloidal gelatinised solution of silver bromide. This coating is carried out in a dark room.

(ii) The sensitive film is loaded in a camera. The image of the object falls on the sensitive film when the shutter of the camera is opened for a moment. During photographic exposure, decomposition of  $\text{AgBr}$  occurs to form minute particles of silver.

(iii) The film is now developed in the dark by adding a developer which acts as a reducing agent. The developer is an alkaline solution of which reduces some of the silver bromide to black silver. The rate at which silver is formed in this process depends upon the intensity of light during the exposure period. The darker parts of the film are those which got the greatest illumination. As there will be unreacted  $\text{AgBr}$  on the film, the film is developed in the dark to prevent a general blackening of the picture. The image is made visible during this process. However, the brightest parts of the object are shown as the darkest in this picture. For example, the face of a person will look dark and his hair will look grey. It is for this reason that the developed picture is called a **NEGATIVE**.

(iv) The film is now fixed by dipping it in sodium thiosulphate (hypo) solution which removes the unchanged silver bromide as a complex ion.



This step is also carried out in darkness. After washing the film with hypo solution, the film can be handled in daylight.

(v) A positive print is then obtained by shining light through the negative on a photographic paper which also contains AgBr. The negative image is reversed and the dark areas on the negative subsequently become the light areas on the print and vice versa.

Development and fixing are now carried out in similar way to that used for the negative

### 15 3 ZINC AND MERCURY (Zn and Hg)

Zinc and mercury belong to group 12 of the periodic table. Some general properties of these elements are given in Table 15 5

TABLE 15 5

Some General Properties of Zinc and Mercury

Element	Atomic number	Electronic configuration	Atomic radius (pm)	Ionic radius $M^{2+}$ (pm)	<i>m p</i> (K)	<i>b.p</i> (K)	Density $g\ cm^{-3}$	Oxidation states
Zinc (Zn)	30	[Ar] $3d^{10}4s^2$	125	74	692	1180	7.1	+2
Mercury (Hg)	80	[Xe] $5d^{10}6s^2$	144	110	234	630	13.6	+1, +2

Zinc and mercury do not exhibit oxidation states in which the d-electrons are involved. They are, therefore, considered to be non-transition metals. They, however, form ions and complexes in the +2 oxidation state by losing  $ns^2$  electrons.

#### 15 3 1 Occurrence and Extraction

The principal ore of zinc is ZINC BLENDE,  $ZnS$ . The other ores are CALAMINE,  $ZnCO_3$ , and ZINCITE,  $ZnO$ . In India, zinc blende is mined in Zawar mines located near Udaipur in Rajasthan.

Zinc blende, after concentration by floatation, is roasted in air to convert it into oxide. Sulphur dioxide so formed is used in the manufacture of sulphuric acid. In the case of calamine ore, calcination of the ore is carried out instead of roasting. The oxide obtained is mixed with crushed coke and heated to 1673 K in a fire clay retort where it is reduced to Zn metal. Being volatile at this temperature, the metal distills over and is condensed. The metal is refined by fractional distillation or by electrolysis.

Zinc dust is prepared by atomising molten zinc with a blast of air. Granulated zinc is prepared by pouring molten zinc into cold water.

The only important ore of mercury is the sulphide ore mercuric sulphide,  $HgS$ . It is found mainly in Spain and Italy. Mercury is extracted from the sulphide ore by heating it in air at 773K-873K. The mercury vapour evolved in the process is

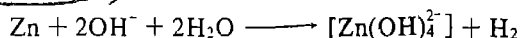


condensed to the liquid metal (about 99.7% pure) Mercury so obtained contains lead, zinc and tin as impurities. It is purified by passing it slowly through dilute  $\text{HNO}_3$ . Mercury (I) nitrate is formed to some extent in this process and reacts with the metals present as impurities leaving pure mercury. Mercury is best purified by distillation under reduced pressure.

### 15.3.2 Properties of Zn and Hg

Zinc is more reactive than mercury. Zinc is a good conductor whereas mercury has relatively low thermal and electrical conductivity. Mercury is a liquid at room temperature because of the weak interatomic forces. Mercury forms the  $\text{Hg}_2^{+2}$  ion in the form  $\text{Hg}_2^{+2}$  in which two mercury atoms are covalently bonded. Most metals dissolve in mercury forming amalgams. Zinc is readily oxidised to  $\text{ZnO}$  whereas Hg is only slowly oxidised near its boiling point to form  $\text{HgO}$ . Pure zinc does not react with water but impure zinc decomposes steam quite readily with the evolution of  $\text{H}_2$ . Mercury is not attacked by water or steam. Pure zinc does not react with dilute non-oxidising acids ( $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ ), but the impure metal is attacked by these acids forming its  $2+$  ions and liberating hydrogen. Mercury is not attacked by dilute non-oxidising acids. Both zinc and mercury react with hot, concentrated  $\text{H}_2\text{SO}_4$  to form the corresponding sulphates. The reaction of Zn and Hg with nitric acid depends upon the temperature and the concentration of the acid. Dilute, warm nitric acid liberates nitric oxide on reaction with Zn and Hg whereas hot, concentrated  $\text{HNO}_3$  gives out nitrogen dioxide.

Zinc reacts with hot sodium hydroxide solution and forms the soluble zincate ion,  $[\text{Zn}(\text{OH})_4]^{2-}$  in solution. Mercury remains unaffected by alkalis.

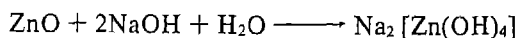


### 15.3.3 Compounds of Zinc and Mercury

#### Oxides

Zinc oxide,  $\text{ZnO}$ , is obtained by burning zinc metal in air or by heating the carbonate or the nitrate.

Zinc oxide is a white solid which is insoluble in water. The colour disappears on cooling. It is soluble in acids and forms the corresponding salts. With alkalis, it forms zincates,  $[\text{Zn}(\text{OH})_4]^{2-}$ .



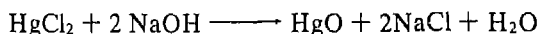
Zinc oxide is reduced to metallic zinc when heated with carbon or hydrogen. It is used as white paint. It is not blackened in hydrogen sulphide. It is used as zinc ointment in medicine, as a glaze in ceramics and as a filler in the rubber industry. It is also used as a catalyst with chromic oxide in the synthesis of methyl alcohol from water gas ( $\text{CO} + \text{H}_2$ ) and hydrogen.

Cr 2 3 7 2 n

#### Mercury (II) oxide

It is obtained as a red solid by heating mercury in excess air for a long time at 623K.

or by heating  $\text{Hg}(\text{NO}_3)_2$  alone or in the presence of Hg. When sodium hydroxide solution is added to a solution of mercury (II) chloride, the yellow precipitate of  $\text{HgO}$  is obtained



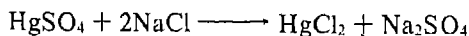
The difference in particle size of  $\text{HgO}$  arises because of differences in particle size as a pigment in oil paints. It is also used as a mild antiseptic in ointments.

#### *Zinc (II) chloride*

A solution of zinc (II) chloride is obtained when Zn metal,  $\text{ZnO}$  or  $\text{ZnCO}_3$  is treated with dilute  $\text{HCl}$ . Crystals of the zinc chloride dihydrate,  $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$  are obtained on evaporating the solution. On further heating, anhydrous  $\text{ZnCl}_2$  is obtained. Zinc chloride is very deliquescent and highly soluble in water. It readily dissolves in organic solvents. It is used as a flux in soldering and as a timber preservative. It is also used in the preparation of vulcanised paper or fibre (used for making fibre boards).

#### *Mercury (II) chloride*

It is formed rapidly when chlorine is brought into contact with Hg. Commercially, it is prepared by heating a mixture of mercury (II) sulphate and sodium chloride and a small amount of manganese oxide which oxidises any  $\text{Hg(I)}$  salt formed during the reaction

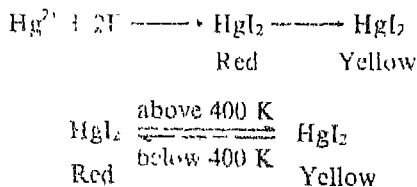


It is a white crystalline solid, sparingly soluble in cold water, but soluble in hot water. It is readily soluble in organic solvents, such as ethanol and ether (suggesting its covalent nature). Mercury (II) chloride is reduced to mercury (I) chloride and then to Hg when a tin (II) chloride solution is added to mercury (II) chloride.

Mercury (II) chloride is poisonous. Its best antidote is the white of an egg which gives an alternative protein material for it to act upon. A very dilute solution of mercury (II) chloride is sometimes used as an antiseptic (for sterilising the hands).

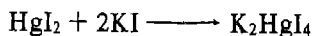
#### *Mercury (II) iodide*

It precipitates as a yellow solid which rapidly turns red when a requisite amount of potassium iodide solution is added to a solution of mercury (II) chloride.



Mercury (II) iodide readily dissolves in an excess of potassium iodide solution and

forms the  $(\text{HgI}_4)^{2-}$  complex ion



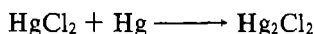
An alkaline solution of  $\text{K}_2\text{HgI}_4$  is called Nessler's reagent which is used to test the presence of ammonia or ammonium ion. It gives a brown precipitate.

### Mercury (I) chloride

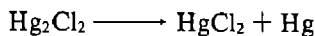
It precipitates out as a white solid when solutions containing a mercury (I) salt and chloride ions are mixed.



It can also be obtained by heating  $\text{HgCl}_2$  and  $\text{Hg}$  in an iron vessel. Mercury (I) chloride,  $\text{Hg}_2\text{Cl}_2$  thus obtained is purified by sublimation



Mercury (I) chloride (called CALOMEL) is a white powder, insoluble in water. It sublimes when heated.

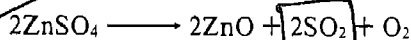


### Sulphides of Zn and Hg

Sulphides of zinc and mercury occur in nature as zinc blende and cinnabar respectively. These are also obtained by passing  $\text{H}_2\text{S}$  gas through solutions of  $\text{Zn}^{2+}$  and  $\text{Hg}^{2+}$ . Zinc sulphide is white while  ~~$\text{HgS}$  is black in colour.~~ Zinc sulphide is soluble in dilute  $\text{HCl}$  and so it is not precipitated by  $\text{H}_2\text{S}$  in an acidic medium. Mercury (II) sulphide is precipitated in an acidic medium.

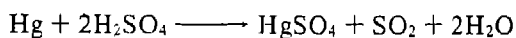
### Sulphates

Zinc sulphate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ), known as WHITE VITRIOL, is prepared by treating metallic zinc, zinc oxide or zinc carbonate (calamine) with dilute  $\text{H}_2\text{SO}_4$ . The solution thus obtained is heated to crystallisation. On heating  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  to  $373\text{K}$ , the six molecules of water of crystallisation are lost and at  $723\text{K}$  it becomes anhydrous. On further heating, the anhydrous salt decomposes.



It is used to prepare lithopone ( $\text{BaSO}_4 + \text{ZnS}$ ), a white pigment. It is also used in galvanising iron and steel.

Mercury (II) sulphate is prepared by treating mercury with concentrated  $\text{H}_2\text{SO}_4$



### MERCURY POISONING AND POLLUTION

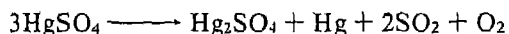
Pollution of the environment by mercury is a cause of great concern because it can enter the blood stream, the digestive system, or the lungs.

Mercury vapour is toxic but since its vapour pressure is low, only prolonged exposure is harmful. Some mercury compounds which are very volatile or soluble, are potential hazards for the human system.

Fortunately, most of the mercury compounds are insoluble. Thus  $\text{HgCl}_2$  is used as a purgative while mercury amalgams are used for dental purposes. Cinnabar, the ore of mercury, is also insoluble and poses no problem.

During eruption of volcanoes, mercury is dispersed in the atmosphere. Burning of coal also does the same. Although mercury is only about 1 ppm in coal, combustion of coal releases about 5000 tons of mercury into the atmosphere every year. In industries producing sodium hydroxide and chlorine by electrolysis, some mercury is regularly lost through waste products into river water where it is consumed by fish and finally by man. More than fifty people died some years ago due to mercury poisoning by eating fish in Minimata, Japan, and many others were seriously affected. The poisoning also caused babies to be born with deformities and brain damage.

It is a white, opaque mass which decomposes on heating to give mercury (I) sulphate.



Some important alloys of Zn are.

(i) Brass (Cu - 70%, Zn - 30%), and (ii) German silver (Cu - 60%, Zn - 30%, Ni - 20%)

#### 15.3.4 Uses of Zinc and Mercury

Zinc being resistant to atmospheric corrosion on account of the formation of basic carbonate on its surface is used for galvanizing. ~~Zinc alloys are used in galvanizing.~~

Mercury is used in the preparation of calomel which is used to prepare a standard electrode. It is used in making thermometers and barometers. Mercury amalgams are used as dental filling especially with gold and silver. The amalgams are also used as catalysts in carrying out certain chemical reactions.

## 15.4. TIN AND LEAD (Sn AND Pb)

Tin and lead have been known to man since time immemorial. In early days, these two metals were not always distinguished from each other. They are at the bottom of group 14 in the periodic table. Some general properties of these metals are given in Table 15.6

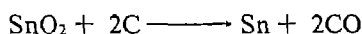
TABLE 15.6

Some General Properties of Tin and Lead

Element	Atomic Number	Electronic configuration	Atomic radius (pm)	Ionic radius $M^{2+}$ (pm)	radius $M^{4+}$ (pm)	Density $g\ cm^{-3}$	m.p. (K)	b.p. (K)	Oxidation States
Tin (Sn)	50	$3d^{10}4d^{10}5s^25p^2$	141	112	71	7.29	505	2960	+2, +4
Lead (Pb)	82	$4f^{14}5d^{10}6s^26p^2$	151	120	84	11.34	600	2024	+2, +4

## 15.4.1 Occurrence and Extraction of Tin

Tin is extracted from its common ore, CASSITERITE,  $SnO_2$ . The crushed ore is washed with water to remove lighter impurities. The ore is then roasted to remove arsenic and sulphur as volatile oxides. Tin is obtained by reducing it with coal in a reverberatory furnace. Limestone is added to produce a slag with the impurities which can be removed.

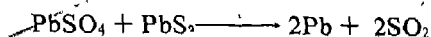
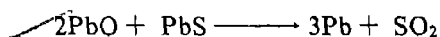
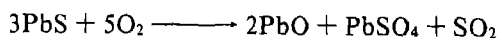


Crude tin so obtained is contaminated with iron and other metals. It is, therefore, remelted on an inclined furnace. The easily fusible tin melts away and the less fusible impurities are left behind. Molten tin is finally stirred to bring it into contact with air. In this process any remaining metal impurities are oxidised forming a scum which rises to the surface and is removed.

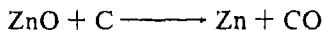
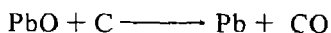
## 15.4.2 Occurrence and Extraction of Lead

The principal ore of lead is GALENA,  $PbS$ , often found in association with zinc blende,  $ZnS$ . Lead is also found as ANGLESITE,  $PbSO_4$  or CERUSSITE,  $PbCO_3$ . In India, small quantities of lead ores are found at Panjori in Sawai Madhopur, Jaipur and in Chitral (near Udaipur).

Galena is roasted in air to convert it into lead oxide ( $PbO$ ) and lead sulphate ( $PbSO_4$ ). Some galena is also not changed. In this case, supply of air is not allowed, the unreacted  $PbS$  reacts with  $PbO$  and  $PbSO_4$  to produce lead metal.



In another method, the mixed sulphides ( $\text{PbS}$  and  $\text{ZnS}$ ) are roasted to obtain oxides. The mixed oxides are fed into a blast furnace with coke. These oxides are then reduced to their respective metals



Molten lead is tapped from the bottom of the furnace. Zinc vapour which comes out from the top of the furnace is condensed. Zinc being less dense than lead, forms the upper layer and can be removed.

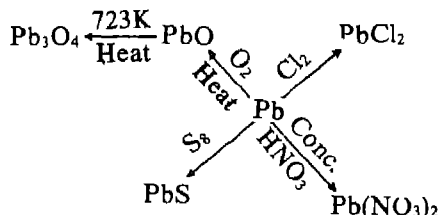
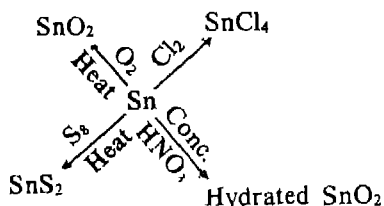
Crude lead is further purified by removing copper, silver, gold, antimony and arsenic with the aid of suitable methods.

### 15.4.3. Properties of Tin and Lead

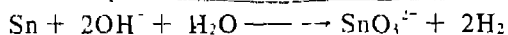
Tin is a soft silvery white metal. It is ductile and can be rolled into thin sheets (tin foils). Ordinary white tin is not attacked by air or water at ordinary temperatures; on heating in air it forms tin oxide,  $\text{SnO}_2$ .

Lead, when exposed to air, is a bluish-grey and lustrous metal but soon gets covered with a thin layer of lead hydroxide,  $\text{Pb(OH)}_2$ , and lead carbonate,  $\text{PbCO}_3$  and acquires a dull appearance. Lead can be rolled and shaped into pipes.

Some of the important reactions of tin and lead are given below:



Dilute  $\text{HCl}$  has little effect on lead. Hot concentrated alkalis react with tin to form the stannate ion. Lead forms plumbate ion in which lead is divalent



### 15.4.4 Uses of Tin and Lead

- (i) Tin is widely used in plating iron to resist corrosion. Tin plating is done by electrolytic deposition of tin on an iron article to be plated (cathode) using acidified tin sulphate,  $\text{SnSO}_4$ , as the electrolyte.
- (ii) Tin foils are used for making food containers.
- (iii) Several important alloys contain tin.

Lead is mainly used

- (i) to make cable coverings;
- (ii) to make bullets, shots and lead accumulators;
- (iii) to make pigments such as red lead, white lead, chrome yellow and chrome red;
- (iv) to prepare lead tetraethyl,  $(\text{C}_2\text{H}_5)_4\text{Pb}$ , which is used as an additive to petrol to prevent 'knocking'.

## Some Important Alloys of Sn and Pb

Alloy	Percentage composition	Uses
Soft solder	Pb- 50, Sn - 50	Soldering
Type metal	Pb- 70, Sb- 20, Sn - 10	Printing type
Pewter	Pb- 20, Sn- 80	Making utensils

## 15 4 5. Compounds of Tin and Lead

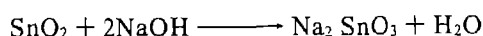
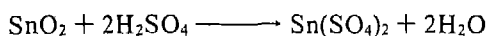
Tin and lead form both divalent, Sn (II) and lead (II) and tetravalent, tin (IV) and lead (IV), compounds

Lead (II) compounds are more stable than lead (IV) compounds. Tetravalent compounds of these elements are generally covalent whereas many of the divalent compounds are essentially ionic

Oxides

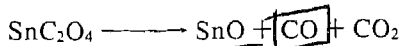
Tin (IV) oxide (stannic oxide) occurs naturally as cassiterite,  $\text{SnO}_2$ . It may be obtained by heating the element in oxygen or by treating it with concentrated  $\text{HNO}_3$

Tin (IV) oxide is an amphoteric oxide. It reacts with concentrated sulphuric acid to form tin (IV) sulphate. It may be fused with sodium hydroxide to give sodium stannate

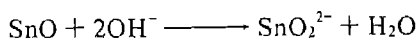
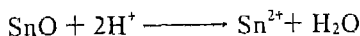


Tin (IV) oxide finds use as a polishing powder, and in glass and pottery manufacture

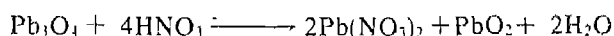
Tin (II) oxide,  $\text{SnO}$ , is obtained by heating tin (II) oxalate



The presence of CO prevents the oxidation of SnO to  $\text{SnO}_2$ . It is a black solid and amphoteric in nature.

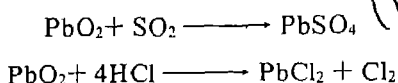


Lead (IV) oxide,  $\text{PbO}_2$ , is formed by treating tri lead tetraoxide,  $\text{Pb}_3\text{O}_4$ , with dilute  $\text{HNO}_3$



Tri lead tetraoxide,  $\text{Pb}_3\text{O}_4$  behaves as a mixture of  $\text{PbO}_2$  and  $\text{PbO}$ . It is a brown solid. It is a powerful oxidising agent.

Lead (IV) oxide,  $\text{PbO}_2$ , combines vigorously with  $\text{SO}_2$  to form lead (II) sulphate. It also liberates  $\text{Cl}_2$  from concentrated HCl when warmed



Like  $\text{SnO}_2$ , lead (IV) oxide is amphoteric. It reacts with  $\text{HCl}$  to form lead (IV) chloride which readily decomposes to lead (II) chloride and  $\text{Cl}_2$ . It also reacts with alkalis to give plumbates (IV),  $\text{PbO}_3^{2-}$ . Lead (IV) oxide is used in lead acid batteries (accumulators).

Lead (II) oxide,  $\text{PbO}$ , exists in red and yellow forms. It can be made by heating lead (II) carbonate and lead (II) nitrate.

Trilead tetraoxide,  $\text{Pb}_3\text{O}_4$ , can be prepared by heating lead (II) oxide in air at 673K.



On further heating,  $\text{Pb}_3\text{O}_4$  decomposes at 773 K into lead (II) oxide and oxygen

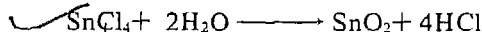
### Sulphides

Tin (II) sulphide and lead (II) sulphide are precipitated when  $\text{H}_2\text{S}$  is passed through a solution of their salts. Tin (II) sulphide,  $\text{SnS}$ , is a dark brown solid and  $\text{PbS}$  is a black solid. Tin (II) sulphide is soluble in a solution of ammonium polysulphide,  $(\text{NH}_4)_2\text{S}_x$ , whereas  $\text{PbS}$  is insoluble.

### Halides

Tin (II) fluoride,  $\text{SnF}_2$ , is prepared by dissolving  $\text{SnO}$  in hydrofluoric acid,  $\text{HF}$ . It is used as an ingredient in toothpastes to decrease dental decay. Tin (II) chloride,  $\text{SnCl}_2$ , is formed by dissolving tin in concentrated  $\text{HCl}$ . On cooling, crystals of tin (II) chloride dihydrate,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , separate out. Anhydrous  $\text{SnCl}_2$  is prepared by heating tin in a current of  $\text{HCl}$  vapour.

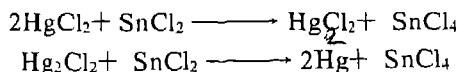
Tin (IV) chloride,  $\text{SnCl}_4$ , is made by passing  $\text{Cl}_2$  over the metal. It is a colourless liquid which fumes in moist air due to hydrolysis.



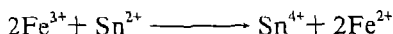
Tin (IV) chloride is covalent, similar to  $\text{CCl}_4$ , and is soluble in organic solvents. Although it is hydrolysed by water, a definite hydrate ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ) can be isolated from hydrochloric acid solution. With an excess of  $\text{HCl}$ ,  $\text{SnCl}_4$  forms hexachlorostannic acid.



Tin (II) chloride,  $\text{SnCl}_2$ , which is more stable than  $\text{SnCl}_4$ , is a powerful reducing agent. It reduces mercury (II) chloride, first to white insoluble mercury (I) chloride and then to mercury.



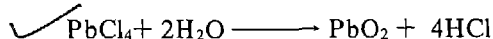
It also reduces iron (III) salts to the iron (II) state.



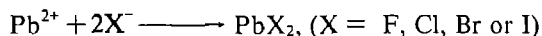


This reaction provides a method for estimating iron (III), the Fe(II) formed is titrated with a potassium permanganate solution

Lead forms lead tetrafluoride,  $\text{PbF}_4$ , and lead tetrachloride,  $\text{PbCl}_4$ . Lead tetrafluoride is an ionic solid whereas  $\text{PbCl}_4$  is a covalent liquid. Lead tetrachloride,  $\text{PbCl}_4$ , is formed when  $\text{PbO}_2$  is dissolved in concentrated  $\text{HCl}$  at 273 K. It is rapidly hydrolysed by water



Lead (II) halides are stable.  $\text{PbCl}_4$ , in fact, decomposes to  $\text{PbCl}_2$  and  $\text{Cl}_2$ . Lead (II) halides are sparingly soluble solids and are easily prepared by adding halide ions to a soluble lead (II) salt



The ionic character of these halides decreases as the atomic number of the halogen increases. All the halides, except  $\text{PbI}_2$  which is yellow in colour, are white solids.

The formation of  $\text{PbCl}_2$  and  $\text{PbI}_2$  serves as a test for  $\text{Pb}^{2+}$  in qualitative analysis. Both are more soluble in hot water than in cold. On cooling, they separate out in crystalline form.

## EXERCISES

- 15.1 How are the three different forms of iron—pig iron, wrought iron and steel different from each other?
- 15.2 Briefly discuss the chemical reactions which occur in a blast furnace during the extraction of iron from haematite
- 15.3 How is pure copper extracted from copper pyrites? List two physical properties and two uses of copper
- 15.4 How is copper sulphate pentahydrate obtained? What is the effect of heat on it?
- 15.5 For copper describe briefly
  - (i) how you would prepare a compound of the metal in its lowest oxidation state,
  - (ii) how you would prepare a compound of the metal in its highest oxidation state;
  - (iii) one use of the salt described in (ii)
- 15.6 Describe briefly how a sample of copper (I) chloride may be prepared. Explain the disproportionation reaction of  $\text{Cu (I)}$  ion
- 15.7 How are silver halides prepared? How would you test the presence of these halide ions with ammonia solution? Describe briefly the use of  $\text{AgBr}$  in photography
- 15.8 How and under what conditions does copper react with  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ ? Describe the preparation of copper (II) chloride dihydrate
- 15.9 Give an account of the extraction of silver by the cyanide process. Describe briefly how a pure sample of silver is obtained electroanalytically

- 15.10 What do you mean by noble metals? Name the noble metals which you know. List two physical and chemical properties of copper, silver and gold. Write down the uses of some important alloys of copper.
- 15.11 Give a brief account of the extraction and properties of zinc. How are zinc (II) chloride and zinc (II) sulphate prepared. Mention the important properties and uses of these two compounds.
- 15.12 Give an account of the occurrence, extraction and purification of mercury. Describe the reactions which occur when an aqueous solution of mercury (II) chloride is treated with.
- (i) an aqueous solution of potassium iodide,
  - (ii) an aqueous solution of tin (II) chloride,
  - (iii) copper,
  - (iv) an aqueous solution of sodium hydroxide.
- What peculiar behaviour does mercury have?
- 15.13 How is lead extracted from galena ore. Write equations for the reactions which occur during the process of extraction.
- 15.14 List two physical and two chemical properties of tin and lead.
- 15.15 Mention two alloys of lead and tin and their uses.
- 15.16 Write down the reaction in parting between Ag and  $\text{H}_2\text{SO}_4$  as well as Ag and  $\text{HNO}_3$ .

## UNIT 16

### STRUCTURE AND SHAPE(S) OF HYDROCARBONS

*Nature is left handed. Molecules can  
be both left-and right-handed.*

#### OBJECTIVES

In this Unit, we shall learn

- \* the classification of hydrocarbons into: (i) alkanes (ii) alkenes, (iii) alkynes, and (iv) arenes,
- \* the structural features of different types of hydrocarbons,
- \* different types of isomerism like structural isomerism, conformational isomerism and stereoisomerism

THE SIMPLEST ORGANIC COMPOUNDS are hydrocarbons, containing carbon and hydrogen only. In nature, hydrocarbons occur chiefly in coal, natural gas and petroleum. All organic compounds can be thought of as derived from hydrocarbons, obtained by substituting hydrogen with an appropriate functional group (see Unit 7 for a discussion of functional groups). Based upon their structure and chemical reactivity, hydrocarbons can be broadly classified into four types: (i) alkanes, (ii) alkenes, (iii) alkynes, and (iv) arenes. This classification is based upon the nature of bonds between carbon atoms. An alkane contains only carbon-carbon single bonds, an alkene has at least one carbon-carbon double bond and an alkyne at least one carbon-carbon triple bond. Arenes have special structural features which will be discussed in detail later in this Unit. Alkanes are also known as saturated hydrocarbons as they have only carbon-carbon single bonds. Alkenes, alkynes and arenes are collectively called unsaturated hydrocarbons as they have at least one carbon-carbon multiple (or unsaturated) bond. While the first three types can be either acyclic or cyclic, all arenes are cyclic compounds.

### 16.1 ALKANES

Alkanes or saturated hydrocarbons are also known as paraffins (from Latin, meaning little affinity or reactivity). The general formula of an acyclic alkane is  $C_nH_{2n+2}$ . Cycloalkanes can be represented by the general formula  $C_nH_{2n}$  (if they are monocyclic) or  $C_nH_{2n-2}$  (if they are bicyclic) and so on. Alkanes contain only carbon-carbon single bonds and carbon-hydrogen bonds. The formation of only single bonds requires that each carbon in an alkane be  $sp^3$  hybridised. As a carbon atom is tetravalent, and in an alkane also,  $sp^3$  hybridised, the four bonds that it forms are directed towards the four corners of a tetrahedron. Using the simplest alkane, methane ( $CH_4$ ), as an example, it can be seen that the carbon atom is located in the middle of a tetrahedron. The four hydrogens are at the four corners or vertices of the tetrahedron. Each face of the tetrahedron is an equilateral triangle and has three hydrogen atoms. All this is shown in Fig 16.1 (a). For convenience, methane is usually represented as in Fig 16.1 (b) or Fig 16.1 (c). In figure 16.1 (b), the thick, heavy line indicates a C-H bond projecting towards the reader, the normal line, a

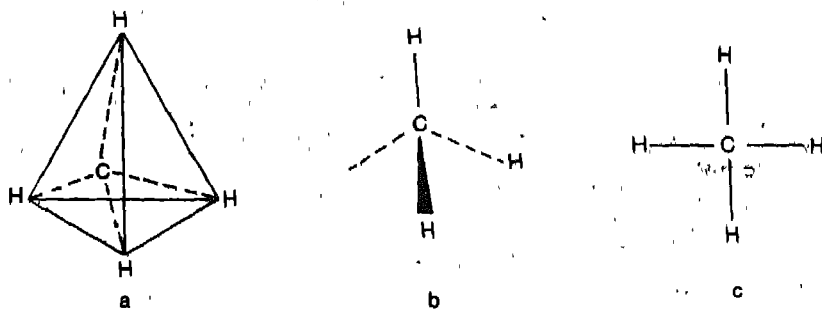
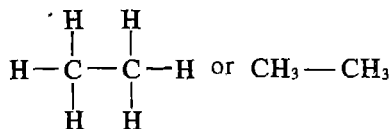
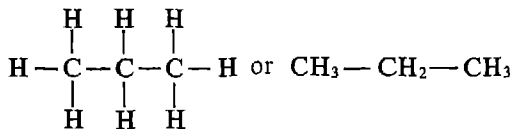


Fig 16.1 Spatial formula of methane

C-H bond in the plane of the page, and the two dotted lines, C-H bonds, projecting behind the plane of the page. Fig 16.1 (c) shows the two dimensional representation of methane. It does not bring out the tetrahedral geometry of methane. For most purposes, structures as in Fig 16.1 (c) will be used as they are easy to draw. However, it must always be remembered that the structure shown in figure 16.1 (c) is a simplification of the real structure given in figure 16.1 (b). In a similar way, ethane ( $C_2H_6$ ) and propane ( $C_3H_8$ ) can be depicted as follows:



ethane

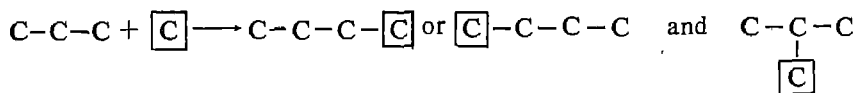


propane

A further abbreviation is possible by writing ethane as  $\text{CH}_3-\text{CH}_3$  and propane as  $\text{CH}_3-\text{CH}_2-\text{CH}_3$ .

### 16.1.1 Structural Isomerism

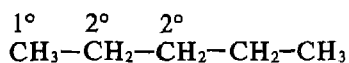
The next hydrocarbon,  $C_4H_{10}$ , can have two different structures. This is because the fourth carbon can be added to propane at either of the two end carbons or to the middle carbon as shown below.



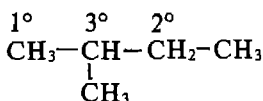
butane

2-methylpropane

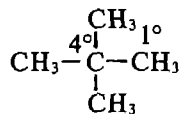
As the two compounds are different but have the same structural formula, butane and 2-methylpropane (iso-butane) are called structural isomers. In a similar way, it can be seen that  $C_5H_{12}$  has three possible structural isomers. With increase in



pentane



2-methylbutane



2,2-dimethylpropane

the number of carbon atoms the number of structural isomers possible for a given molecular formula also increases. For example,  $C_{10}H_{22}$  has 75 structurally isomeric forms.

The carbon atoms present in a compound are classified according to the number of carbons to which they are directly connected. If a carbon atom is bonded to only

one other carbon or to none, it is called a primary carbon (denoted by  $1^0$ ). Similarly, a secondary carbon ( $2^0$ ), is bonded to two carbons, a tertiary ( $3^0$ ) to three and a quaternary ( $4^0$ ) to four.

### 16.1.2 Conformation in Hydrocarbons

The carbon-carbon single bond in ethane is a  $\sigma$  bond and has cylindrical symmetry about the internuclear axis. It is thus possible to rotate one methyl group of ethane about the carbon-carbon bond keeping the other fixed, without affecting the  $\sigma$  bond. The different structures which can be produced by this rotation are called **CONFORMERS**. The molecular geometry corresponding to a conformer is known as **conformation**. Although an infinite number of conformations are possible for ethane, only two are important and are shown in figure 16.2. In the eclipsed conformation, all

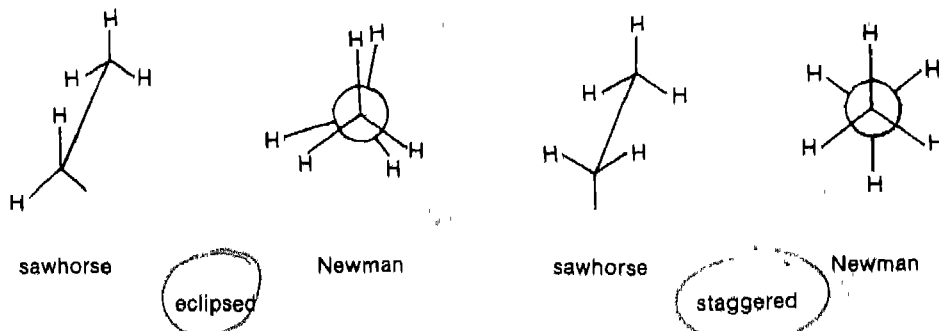


Fig. 16.2 Eclipsed and staggered conformations of ethane

the C-H bonds of one methyl group are aligned with those of the second and in the staggered form the two methyl groups are rotated as far away as possible from one another. The staggered conformer is more stable than the eclipsed conformer by about  $12.6 \text{ kJ mol}^{-1}$ . As this energy difference is small, there is no effective energy barrier to rotation about a  $\sigma$  bond. Another way of expressing this is to say that there is 'free rotation' about a  $\sigma$  bond. At room temperature, the eclipsed and staggered forms of ethane interconvert rapidly and cannot be isolated as separate conformers.

Conformers are usually represented using either the Sawhorse projection or the Newman projection. Of the two, the Newman projection is easier to draw and visualise. To convert a conformer from a sawhorse or structural form to the Newman form, the following procedure is adopted. The two carbons forming the  $\sigma$  bond are represented by two circles, one behind the other, so that only the front carbon is seen. The hydrogen atoms attached to the front carbon are depicted by C-H bonds from the centre of the circle. The C-H bonds of the back carbon are drawn from the circumference of the circle.

Conformational isomerism is possible in ring systems as well. While cyclopropane and cyclopentane have planar and almost planar carbon networks, respectively, cyclopentane and cyclohexane do not have all the carbons coplanar. Compared to the normal bond angle of  $109^{\circ} 28'$  for an  $sp^3$  hybridised carbon, cyclopropane has a  $\text{CCC}$  angle of  $60^{\circ}$ , making the molecule very strained and reactive. Cyclobutane, with an angle of  $90^{\circ}$ , is less strained than cyclopropane. In cyclopentane, the angle of  $108^{\circ}$  (that of a regular pentagon) is close to the tetrahedral angle of  $109^{\circ} 28'$  and the molecule has an almost planar conformation. Cyclohexane avoids this strain by assuming conformations in which the bond angles are all close to  $109^{\circ} 28'$  and is therefore quite stable and unreactive. The two most important conformations for cyclohexane are the chair and the boat forms shown in Fig 16.3

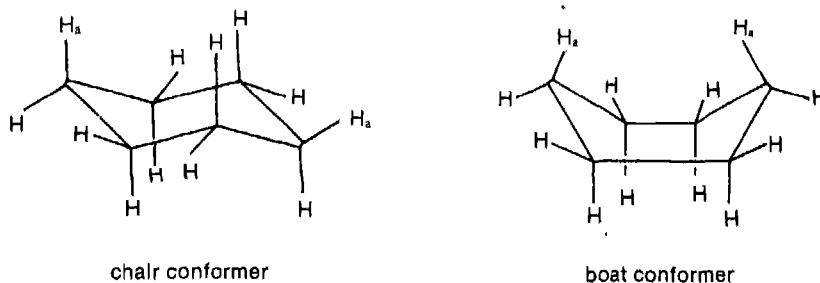


Fig. 16.3 Chair and boat conformations of cyclohexane

Of the two, the chair form is more stable than the boat form, the energy difference being about  $44 \text{ kJ mol}^{-1}$ . This is because in the boat form, many hydrogens on adjacent carbons correspond to the unfavourable eclipsed conformation of ethane. Also, the two hydrogens marked  $H_a$  in the boat form in Fig 16.3 are quite close and repel one another. On the other hand, the chair form does not have these unfavourable interactions and the hydrogens all correspond to the more stable staggered conformation of ethane.

## 16.2 STEREOISOMERISM AND CHIRALITY

In addition to the two types of isomerism discussed earlier (structural and conformational), alkanes also exhibit isomerism due to different spatial arrangements of atoms or groups in a molecule. Such an isomerism is known as STEREISOMERISM (stereo means 'space' in Greek) and is of two types: (i) optical isomerism, and (ii) geometrical isomerism. Geometrical isomerism will be discussed in detail in section 16.3

An object which is non-superimposable on its mirror image is said to be CHIRAL. Common, everyday examples are a pair of hands, a pair of shoes, a pair of gloves

and some of the letters of the alphabet like P, F and J. The word 'chiral' is derived from the Greek word for hand and the property of being chiral is known as CHIRALITY. Achiral objects are those which are superimposable on their mirror images. Examples include a sphere, a chair and alphabets like A, O and M. A chiral and achiral example is illustrated in Fig. 16.4. Any object which is non-superimposable on its mirror image and hence chiral, is also known as a disymmetric object.

Many organic compounds are disymmetric. First, the reasons why they are disymmetric have to be understood. Secondly, since individual molecules of organic compounds cannot be directly seen, a method is necessary to find out those compounds which are disymmetric.

### 6.2.1 Origin of Chirality

Van't Hoff and LeBel showed in 1873 that the origin of disymmetry in carbon compounds is due to the tetrahedral nature of carbon. They considered various possibilities and concluded that all the experimental results available at that time could be explained by assuming that a saturated carbon forms four bonds directed towards the corners of a tetrahedron. Using methane and its derivatives as examples, it can be easily seen that disymmetry is possible only if four different atoms or groups are attached to the carbon atom. Such a carbon is known as an asymmetric carbon. A molecule like fluorochlorobromomethane is chiral and disymmetric. It cannot be superimposed on its mirror image as shown in Fig. 16.5. As the spatial

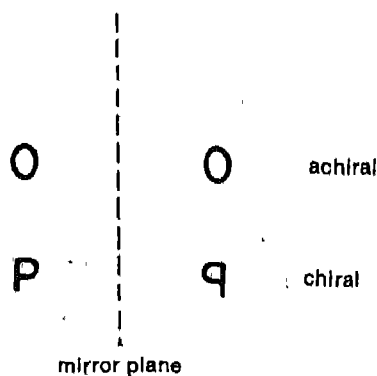


Fig. 16.4 Chiral and achiral objects

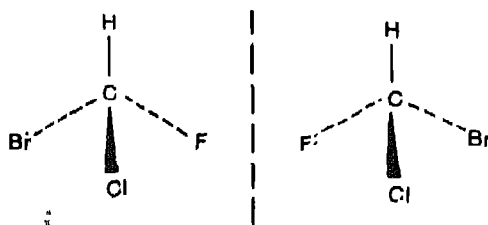


Fig 16.5 Enantiomeric forms of fluorochlorobromo methane

arrangements of atoms in the object and its mirror image are different, they are isomeric compounds. Such an isomerism is known as stereoisomerism. Stereoisomers which are related to one another as an object and its non-superimposable mirror image are termed enantiomers. Enantiomers show identical physical properties like melting or boiling point, density and refractive index. They differ from one another



in their behaviour towards plane polarised light. This difference is used to determine whether or not a compound is disymmetric.

### 16.2.2 Optical Rotation

Ordinary light is made up of light waves of different wavelengths. By using a prism or diffraction grating, light of a single wavelength, known as monochromatic light, can be obtained. Under ordinary conditions, light waves oscillate in a number of planes passing through the line of propagation. However, if the light waves pass through a Nicol prism, then all the oscillations occur only in one plane. Such a beam of light is called PLANE POLARISED LIGHT. When monochromatic, plane polarised light passes through a disymmetric compound, the plane of polarisation is changed, or 'rotated'. In the case of enantiomers, the plane of polarisation is rotated in equal amounts but in opposite directions. As disymmetric molecules have the ability to change an optical property (plane of polarisation), they are said to be optically active. This kind of stereoisomerism is therefore known as optical isomerism. Fig 16.6 illustrates the phenomenon of optical rotation. The instrument used to measure optical rotation is known as a polarimeter.

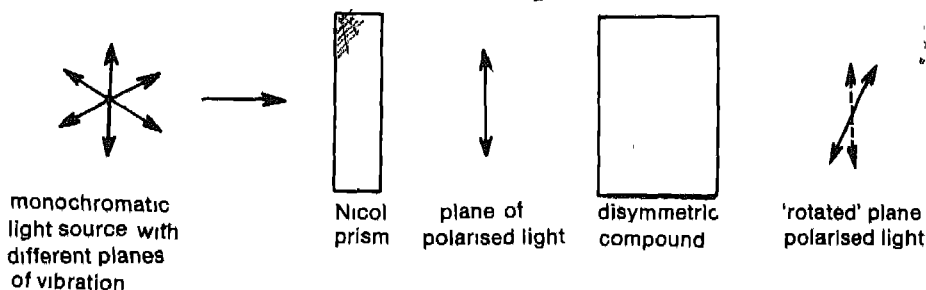


Fig 16.6 Schematic illustration of optical rotation

The enantiomer which rotates the plane of polarisation to the right is called dextrorotatory and is conventionally given a positive sign. Its mirror image, which rotates the plane to the left is termed levorotatory and is designated by a negative sign. Dextro- and levo-isomers are denoted by the letters d- and l-, respectively. The d- and l- forms of 2-butanol are shown in Fig 16.7

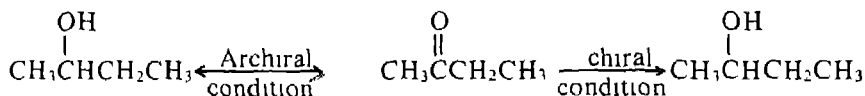


Fig. 16.7 Enantiomeric forms of 2-butanol

Enantiomers display identical chemical reactivity in reactions in which all other conditions are achiral. However, they show different chemical reactivity if even one of the other reaction conditions is chiral. This difference in the reactivity of enantiomers is of great importance in biochemistry and much of the chemistry taking place in our body involves such processes.

### 16.2.3 Racemic Mixture

A mixture containing equal amounts of two enantiomers does not show any optical activity. This is because the two enantiomers present in the mixture have equal but opposite rotations and cancel out one another. Such a mixture is known as a racemic mixture and is denoted by  $dl$  or  $(\pm)$ . Therefore, the absence of optical activity does not mean that the compound is achiral. Thus, for example, if 2-butanone is reduced to 2-butanol under normal conditions, the  $d$ - and  $l$ -forms of 2-butanol will be formed in equal amounts, giving a racemic mixture with no optical rotation. However, the same reaction, if done under special conditions can give either the  $d$ - or the  $l$ -isomer, depending upon the reaction.



Equal amounts  
of  $d$ - and  $l$ -isomers.

$d$ - or  $l$ -isomer

Racemic mixture

Asymmetric synthesis

The product of such a reaction will show optical rotation. A reaction in which one enantiomer is preferentially formed is known as asymmetric synthesis. Most of the reactions occurring in biological systems belong to this category. It is possible to separate a racemic mixture into  $d$ - and  $l$ -enantiomers by suitable methods. This process of separation is known as resolution.

## 16.3 ALKENES

Alkenes are hydrocarbons having a carbon-carbon double bond. Acyclic alkenes with one double bond have the general formula  $C_nH_{2n}$ . Since they have two less hydrogens than the corresponding alkanes, alkenes are also known as unsaturated hydrocarbons, along with alkynes and arenes. An older name for alkenes, still in use, is 'olefins', meaning oil forming.

The presence of a carbon-carbon double bond in an alkene confers on it certain structural features which are absent in the corresponding alkane. A careful look at the structure of ethene, the simplest olefin, brings this out clearly. Each of the two carbons of ethene is  $sp^2$  hybridised and forms three  $\sigma$  bonds, two with two hydrogens

and the third with one another. They are all in the same plane. The  $\pi$  bond between the two carbons is perpendicular to this plane, as shown in Fig. 16.8, and is present *both above and below* the plane. Therefore, a carbon-carbon double bond comprises two different kinds of bonds, a  $\sigma$  bond and a  $\pi$  bond. A  $\sigma$  bond has a symmetry axis along the C-C bond, but a  $\pi$  bond lacks this symmetry. However, the  $\pi$  bond is bisected by the plane containing the  $sp^2$  carbons and the atoms or groups attached to them.

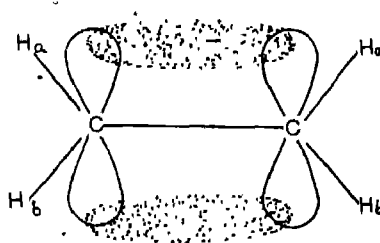


Fig 16.8 The  $\pi$  bond in ethene

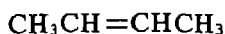
A  $\pi$  bond is not as strong as a  $\sigma$  bond. Thus, for example, the bond energies of a carbon-carbon single bond ( $\sigma$  bond) and a carbon-carbon double bond ( $\sigma$  bond plus a  $\pi$  bond) are 347 and 598 kJ mol<sup>-1</sup>, respectively. However, the  $\pi$  bond is sufficiently strong to prevent free rotation of the two carbons with respect to one another, which form the  $\pi$  bond. As an example, H<sub>a</sub> and H<sub>b</sub> in figure 16.8 cannot exchange places just by rotation of C<sub>1</sub> with respect to C<sub>2</sub> without breaking the  $\pi$  bond. This restricted rotation about a  $\pi$  bond gives rise to geometrical isomerism.

### 16.3.1 Isomerism in Alkenes

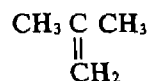
The simplest acyclic alkene which can exhibit isomerism is butene, C<sub>4</sub>H<sub>8</sub>. We have shown the possible isomers of C<sub>4</sub>H<sub>8</sub> here



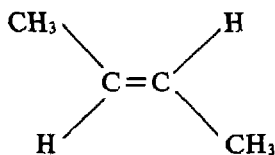
1-Butene



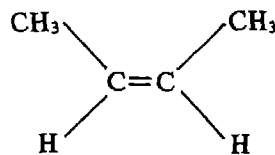
2-Butene



2-Methylpropene

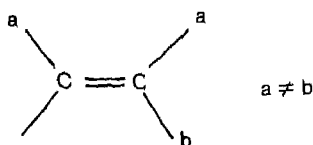


*Trans*-2-butene



*Cis*-2-butene

The three isomers are all structural isomers. Experimentally, however, two isomers of 2-butene are known, having different physical properties. They are the geometrical isomers, *trans*-2-butene (*trans*: opposite side) and *cis*-2-butene (*cis*: same side), respectively. Geometrical isomers are those which cannot be converted to one another due to the absence of free rotation about a double bond. For geometrical isomerism to exist, the following condition should be satisfied:



Where  $a$  and  $b$  are different substituents.

Geometrical isomers are also stereoisomers, as they differ from one another in the way in which the atoms are arranged in space. They differ from optical isomers in that they are not chiral.

Geometrical isomerism plays a very important part in the chemistry of vision. Indeed, the first step in the visual process involves the conversion of the one geometrical isomer into another under the influence of light. Geometrical isomerism is also possible in disubstituted cycloalkanes, but that will not be discussed here.

#### 16.4 ALKYNES

Acyclic alkynes or acetylenes conform to the general formula  $C_nH_{2n-2}$ . As the formula itself implies, they are also unsaturated hydrocarbons. Alkynes have a carbon-carbon triple bond. The two carbons constituting the triple bond in ethyne ( $C_2H_2$ ) are  $sp$  hybridised and form two  $\sigma$  bonds, one with a hydrogen and the second with one another. As shown in Fig.16.9, the  $\sigma$  bonds are all collinear. Two  $\pi$  bonds, mutually

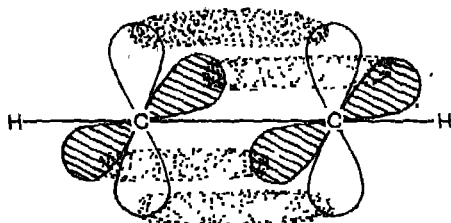


Fig 16.9 The  $\pi$  bond in ethyne

perpendicular to one another, along with the  $\sigma$  bond, together constitute the triple bond. Unlike the single and double bonds, the triple bond by itself does not give rise to any isomerism.

#### 16.5 ARENES

Arenes or aromatic compounds constitute a unique class of unsaturated hydrocarbons. All arenes are cyclic compounds. Monocyclic arenes like benzene ( $C_6H_6$ ) have the general formula  $C_nH_{2n-6}$ , bicyclic arenes like naphthalene ( $C_{10}H_8$ ) conform to  $C_nH_{2n-12}$  and in general, an arene with  $m$  rings has the formula  $C_nH_{2n-6m}$ . Although the molecular formulae indicate that arenes are quite unsaturated, in most chemical reactions arenes behave very differently from alkenes and alkynes. The structures of some simple arenes are given in Fig.16.10.

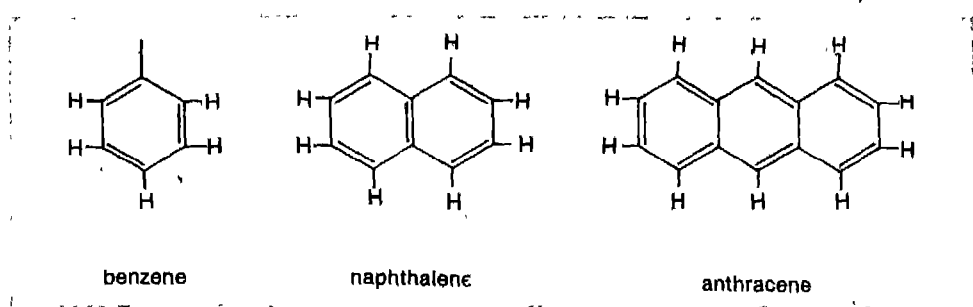


Fig. 16.10 Some simple arenes

### 16.5.1 Structure of Benzene

Elucidation of the structure of the simplest arene, benzene, was one of the the major achievements in the development of chemistry in the nineteenth century. Although the molecular formula of benzene was known as  $C_6H_6$ , no satisfactory structure was proposed till Kekulé in 1865 gave his now famous ring structure. The dream in which Kekulé first came up with this structure is perhaps one of the most important dreams in the history of science. Kekulé's structure of benzene is not without disadvantages. It predicts, for example, that benzene should behave like an alkene and also that it should have alternate single and double bonds, with different bond lengths. Finally, two isomers should result in a 1,2-disubstituted benzene as shown in Fig. 16.11. While Kekulé could not explain the difference in properties between benzene and alkenes based on his structure, he tried to account for the lack of isomers in Fig. 16.11 by postulating a rapid interchange in the position of the double bonds. The proof of the basic correctness of Kekulé's structures, however, became possible after the advent of modern theories of chemical bonding.



Fig. 16.11 Kekulé isomers of 1,2-dichlorobenzene

By employing X-ray diffraction, it could be established that the structure of benzene was a regular hexagon with an angle of  $120^\circ$  and a carbon-carbon bond distance of 139 pm (0.139 nm). This is intermediate to that of carbon-carbon single bond (154 pm) and a carbon-carbon double bond (134 pm). The carbons of benzene are assumed to be  $sp^2$  hybridised, as suggested by the bond angle of  $120^\circ$ . Three  $\sigma$  bonds are formed by each carbon, all in the same plane. The six unhybridised  $\pi$  orbitals (one from each carbon) together have six electrons and are perpendicular to the plane of the  $\sigma$  bonds. All the six  $\pi$ -orbitals together form a  $\pi$  bond above and below the plane of the carbon skeleton, accommodating all the six electrons. Such a  $\pi$  bond, which is spread over more than two carbon atoms, is referred to as a delocalised  $\pi$  bond and is represented by a circle within the hexagon by the six carbons of benzene (Fig. 16.12).

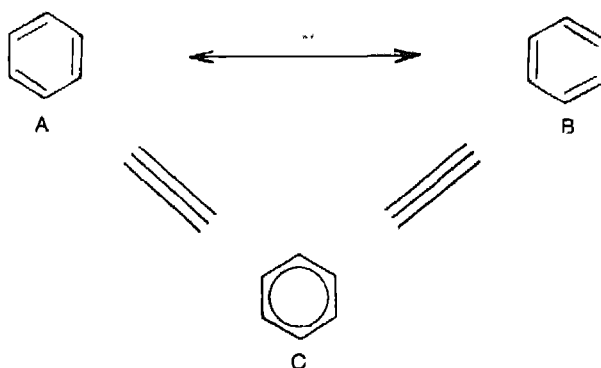


Fig. 16.12 Structure of benzene

This delocalised structure of benzene accounts for the X-ray and the absence of the type of isomerism shown in Fig. 16.11. Furthermore, molecular orbital theory predicts that those cyclic molecules which have alternate single and double bonds with  $4n+2$  ( $n = 0, 1, 2, 3$ , etc.) electrons in the delocalised  $\pi$ -bond are particularly stable and have chemical properties different from other 'unsaturated' hydrocarbons. The delocalisation of  $\pi$  electrons in benzene takes place in a similar way.

### AUGUST KEKULE

Kekule Von Stradonitz Friedrich August, a German chemist was born at Darmstadt, Germany, on 7 September, 1829. He became a Professor at the age of 27 (1856) and a Fellow of the Royal Society in 1875. He made a major contribution to organic chemistry by developing structural theories. He proposed the chain formation in the aliphatic series. Without any access to modern physical techniques for measuring molecular characteristics, Kekule postulated in 1865, two chief structures of benzene molecule having alternate single and double carbon-carbon bonds.



The discovery of the structure of benzene by Kekule was based on a

dream. Here is what Kekulé had to say about his dream.

...again the atoms gambolled before my eyes, but this time the small groups kept demurely in the background. My mind's eye, sharpened by many previous experiences, distinguished larger structures of diverse forms, long series, closely joined together; all in motion, turning and twisting like serpents. But see what was that? One serpent had seized its own tail, and this image whirled defiantly before my eyes. As by a lightning flash, I awoke; and again spent the rest of the night working out the consequences of this idea ..... Let us learn to dream, gentlemen, and then we may find the truth but let us beware of making our dreams public before they have been approved by the waking mind.

Kekulé died in Bonn on 13 July 1896.

### 16.5.2 Resonance

The two structures A and B in Fig. 16.12 (the positions of the double bonds are different in A and B) are known as the resonance or canonical forms of benzene. A resonance or canonical structure is one which is not the correct and is only a convenient (nevertheless incomplete) representation. In the case of benzene, the true structure is neither the resonance structure A nor B but is in between the two and is best represented by C, referred to as a *resonance hybrid*. A note of caution is necessary here. Use of the term 'resonance hybrid' does not mean that C comprises equally of A and B. All that is meant is that the true structure of benzene cannot be readily represented by conventional chemical formulae and is best represented by C and to a lesser extent by A and B. To indicate two structures which are resonance forms of the same compound, a double headed arrow is used, for example  $A \longleftrightarrow B$ . This arrow should be clearly distinguished from that used for an equilibrium ( $\rightleftharpoons$ ). The extra stability which a real molecule has over the hypothetical resonance structure is known as the resonance energy. In the case of benzene, the real molecule is more stable than A or B.

### 16.5.3 Isomerism in Arenes

Arenes exhibit positional isomerism. All monosubstituted benzenes are single isomers, but three different disubstituted benzenes are possible as shown for dimethylbenzene

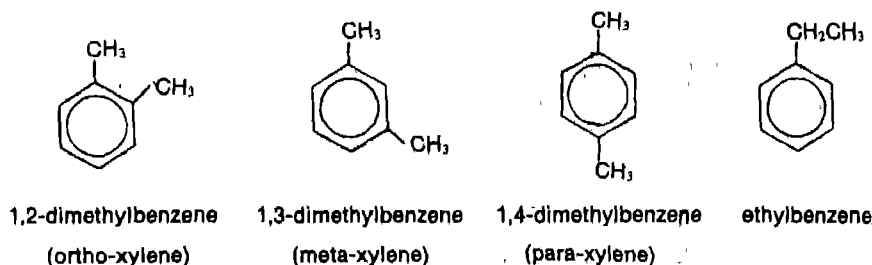


Fig. 16.13 Isomerism in substituted arenes

in Fig.16.13. Ortho-, meta- and para-xylenes are positional isomers. Besides the three possible dimethylbenzenes, a fourth isomer, ethylbenzene, is also known. In the case of naphthalene, even mono-substituted compounds display positional isomerism as in 1-methyl and 2-methylnaphthalene. With higher ring systems, the number of isomers possible also increases.

### EXERCISES

- 16.1 Define the following.  
 (i) Structural isomerism  
 (ii) Stereoisomerism  
 (iii) Conformational isomerism  
 (iv) Positional isomerism
- 16.2 Draw all the possible structural isomers with the molecular formula  $C_6H_{14}$ . Name them.
- 16.3 In the isomers of  $C_6H_{14}$  drawn in question 16.2, indicate primary, secondary, tertiary and quaternary carbons.
- 16.4 Draw the Sawhorse and Newman projections of butane using the C-2 to C-3 bonds as references in  
 (i) eclipsed form  
 (ii) staggered form
- 16.5 Why is cyclopropane very reactive when compared to cyclohexane?
- 16.6 What is the condition to be satisfied for a compound to be chiral?
- 16.7 What is an asymmetric carbon atom?
- 16.8 What are enantiomers? How can they be identified?
- 16.9 In what way does a racemic mixture differ from a chiral compound?
- 16.10 What do you understand by: (i) asymmetric synthesis, (ii) resolution?
- 16.11 What is the origin of geometrical isomerism in alkenes?
- 16.12 Why is it that the carbon-carbon bond distance in benzene is intermediate between a carbon-carbon single and double bond?
- 16.13 What is meant by (i) delocalisation, (ii) resonance energy?
- 16.14 Identify the type of isomerism exhibited by the following compounds:

- (i) 
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{CH}_2-\text{C}-\text{H} \\ | \\ \text{Cl} \end{array}$$
- (ii)  $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$
- (iii)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
- (iv)  $\text{C}_5\text{H}_{12}$



- 16 15 Draw structures to illustrate
- (i) geometrical isomerism
  - (ii) positional isomerism in arenes
  - (iii) a racemic mixture
  - (iv) a chiral isomer of methylpentane,

## UNIT 17

# PREPARATION AND PROPERTIES OF HYDROCARBONS

*We burn more hydrocarbons today than ever before.*

### OBJECTIVES

In this Unit, we shall learn

- \* the principles and processes of isolation of hydrocarbons from two natural sources, namely coal and petroleum;
- \* the industrial processes of preparation of hydrocarbons;
- \* the method of measuring and improving the quality of a fuel,
- \* the laboratory methods for preparation of aliphatic hydrocarbons,
- \* correlation of the variation in physical properties of hydrocarbons with their structures,
- \* chemical reactions of hydrocarbons such as oxidation, addition and substitution;
- \* the reasons for the acidic character of acetylene

DURING THE COURSE of this Unit, we will study the sources, preparation, properties and reactions of hydrocarbons. As we have seen earlier, in Unit 7, hydrocarbons are the parent compounds from which other organic compounds are derived. Replacement of hydrogen atom in a hydrocarbon by an -OH group gives an alcohol, a -COOH group gives a carboxylic acid. Thus, all organic compounds can be derived from hydrocarbons by substituting a hydrogen with a suitable functional group. It is therefore appropriate to commence our study of organic compounds with the study of hydrocarbons.

## 17.1 SOURCES OF HYDROCARBONS

Till the early years of the nineteenth century, the only source of organic compounds was from plants and animals. With the advent of the Industrial Revolution in Europe, fossil fuels like coal and petroleum gained prominence as sources of organic compounds, particularly hydrocarbons. Today, the chief source of hydrocarbons is petroleum. However, in recent years coal is again gaining prominence, due to the uncertain conditions in the world oil market.

### 17.1.1 Origin of Coal and Petroleum

The origin of coal and petroleum (Latin *petra* = rock, *oleum* = oil) is thought to be plant and animal life which flourished long ago. Their burial in the earth's crust for a long time under great pressure in the absence of air resulted in their transformation into coal and petroleum.

While coal is mined like any other mineral, petroleum or crude oil is pumped out by drilling a well. The chief coal producing countries of the world are China, U.S.A., U.S.S.R., U.K., Germany, Poland, Australia and India. Saudi Arabia, Iran, Iraq, the countries in the West Asia, U.S.S.R., U.S.A., U.K., Mexico and China are important oil producing countries. In India, coal is mainly mined in Bihar, West Bengal, Madhya Pradesh and to a lesser extent in Andhra Pradesh. Production in 1984-85 amounted to 147.6 million tonnes and in 1986-87, it was 175.4 million tonnes. The leading oil producing centres are Gujarat, Assam and Bombay High (offshore). In 1986-87, India produced close to 30.5 million tonnes of crude oil.

### 17.1.2 Composition of Coal and Oil

Coal is mainly composed of carbon. Soft coal (bituminous) and hard coal (anthracite) have about 65% and 85% carbon, respectively. Coal also contains arenes (aromatic hydrocarbons) like benzene, toluene, xylene, naphthalene and anthracene besides some organic compounds of sulphur and nitrogen. On the other hand, crude oil is largely made up of aliphatic hydrocarbons with much lesser amounts of aromatic compounds and organic compounds of sulphur and nitrogen.

### 17.1.3 Aromatic Hydrocarbons from Coal

Coal is a commercial source of arenes. When coal is heated in the absence of air to 1270-1675 K (pyrolysis), it is partly broken down into simpler, volatile compounds and a residue, known as coke. The volatile material consists of coal gas, ammonia and a viscous liquid, known as coal tar, which contains aromatic compounds.

Ammonia is removed by absorbing it in acid, and is later converted to ammonium salts. Aromatic hydrocarbons are obtained by fractional distillation of coal tar. The arenes present in coal tar are mainly benzene, toluene, 1, 2-, 1, 3- and 1, 4-dimethylbenzenes (xylenes), naphthalene, anthracene and phenanthrene. Table 17.1 summarises the product obtained by fractional distillation of coal tar. The residue, coke, is used as a reducing agent in metallurgy and as a fuel. Coal gas, which mainly consists of low molecular mass alkanes and alkenes, is also used as a fuel. Although the amount of coal tar and coal gas obtained from coal is small in percentage terms, the large amount of coke produced from coal for industrial use provides significant quantities of coal tar and coal gas.

TABLE 17.1

Fractions of Coal Tar

<i>Number of fractions</i>	<i>Temperature range (K)</i>	<i>Name of fraction</i>	<i>Components</i>
1	Upto 443	Crude light oil	Benzene, toluene, xylene
2	443-503	Middle oil or carbolic oil	phenol
3	503-543	Heavy oil or creosote oil	methyl and higher alkyl
4	543-633	Green oil or anthracene oil	naphthalene, anthracene, phenanthrene
5	—	Pitch	

#### 17.1.4 Hydrocarbons from Petroleum : Oil Refining

The crude oil or petroleum as pumped out of the oil well is a viscous and complex mixture of several hydrocarbons and minor amounts of other compounds. Before it

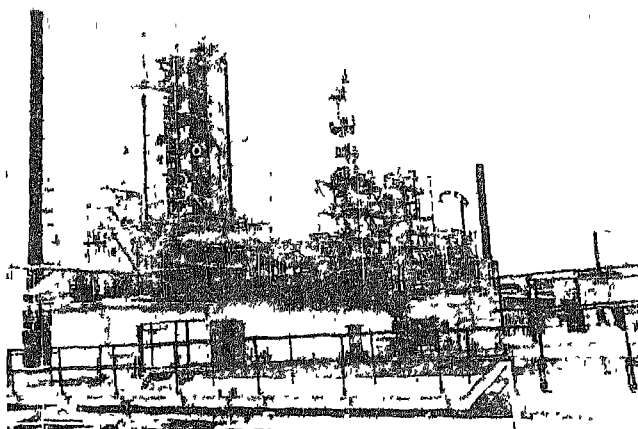


Photo V1 Petroleum refinery

Courtesy PIB, New Delhi

can be used, it has to be purified or 'refined' into different categories. In India, oil refineries are located at Koyali, Bombay, Cochin, Madras, Visakhapatnam, Haldia, Barauni, Guwahati, Dighoi and Mathura.

The first step in the refining process is neutralisation of the crude oil by washing it with acidic or basic solution as needed. The oil is then fractionated by distillation (Unit 18) into several fractions with different boiling ranges. For this purpose, the crude oil is heated in a furnace to 650 K and the pressure reduced. The hydrocarbons so volatilised are fed into the bottom of a bubble tower (Fig 17.1). The bubble tower

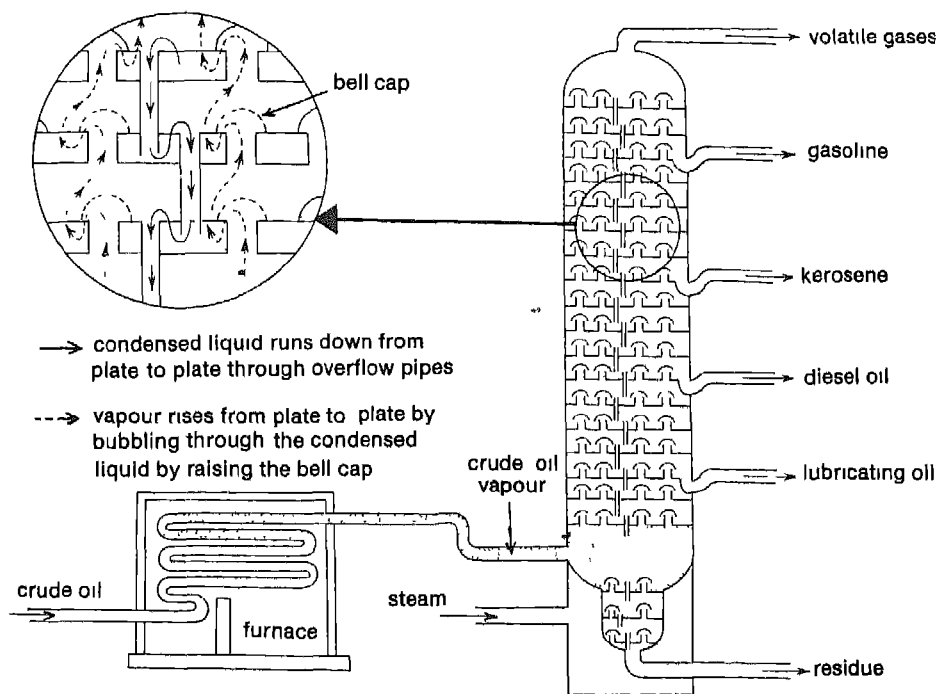


Fig 17.1 Fractional distillation of crude oil. The cutway view shows how fractionation of more volatile components takes place

is a tall cylindrical steel structure with horizontal trays fitted in it. Each tray has a number of holes and a short tube with a bubble cap. The higher boiling fractions condense in the lower portions of the tower. Fractions with lower boiling points rise up the tower and condense at different levels, depending on the boiling points. Thus, several fractions are collected. Each fraction is a mixture of hydrocarbons with a defined boiling range. Gasoline obtained by this procedure is called straight run gasoline. The products of a typical fractionation of petroleum are given in Table 17.2 along with their main uses.

TABLE 17 2  
Typical Fractionation of Petroleum

<i>Fraction</i>	<i>Composition</i>	<i>Boiling range(K)</i>	<i>Approximate %</i>	<i>Uses</i>
Gaseous	C <sub>1</sub> —C <sub>5</sub>	113-303	2	Gaseous fuel, production of carbon black, (hydrogen, and carbon monoxide) used to make ammonia and methanol, gasoline
Petroleum ether (ligroin)	C <sub>5</sub> —C <sub>7</sub>	303-363	2	Solvent used in drycleaning clothes
Gasoline	C <sub>7</sub> —C <sub>12</sub>	343-473	32	Motor fuel
Kerosene	C <sub>12</sub> —H <sub>15</sub>	448-548	18	Illuminant fuel, jet engine fuel
Gas oil, fuel oil and diesel oil	C <sub>15</sub> —C <sub>18</sub>	523-673	20	Furnace fuel, fuel for diesel engines, in cracking
Lubricating oils, greases, petroleum jelly	C <sub>16</sub> and up	623 and up		Lubrication
Paraffin (wax)	C <sub>20</sub> and up	melts (325-330)		Candles, water-proofing, fabrics
Petroleum coke		residue		Artificial asphalt, fuel, electrodes

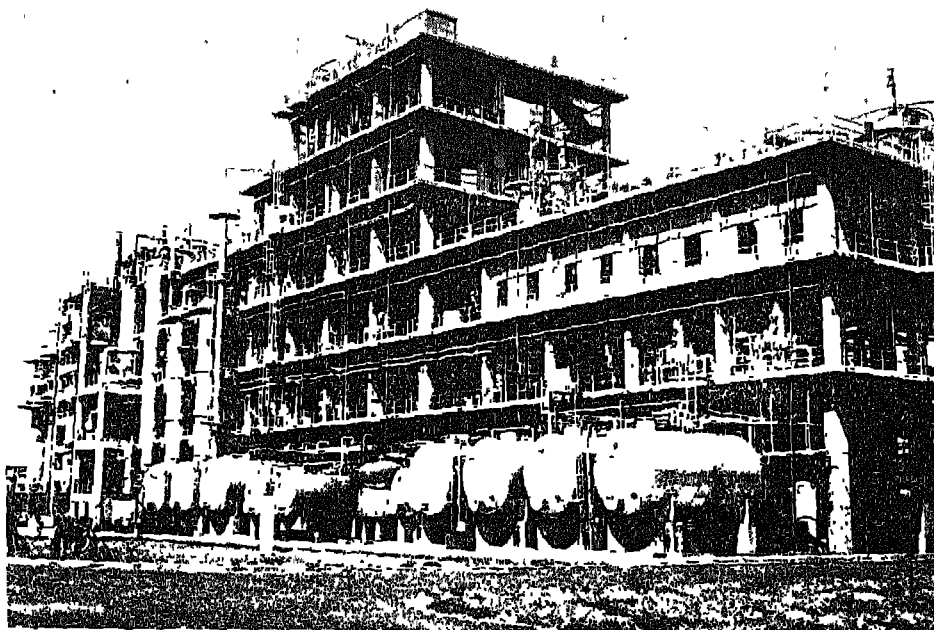


Photo VII Dinethyl terephthalate plant of IPCL's Vadodara complex,

Courtesy IPCL, Vadodara

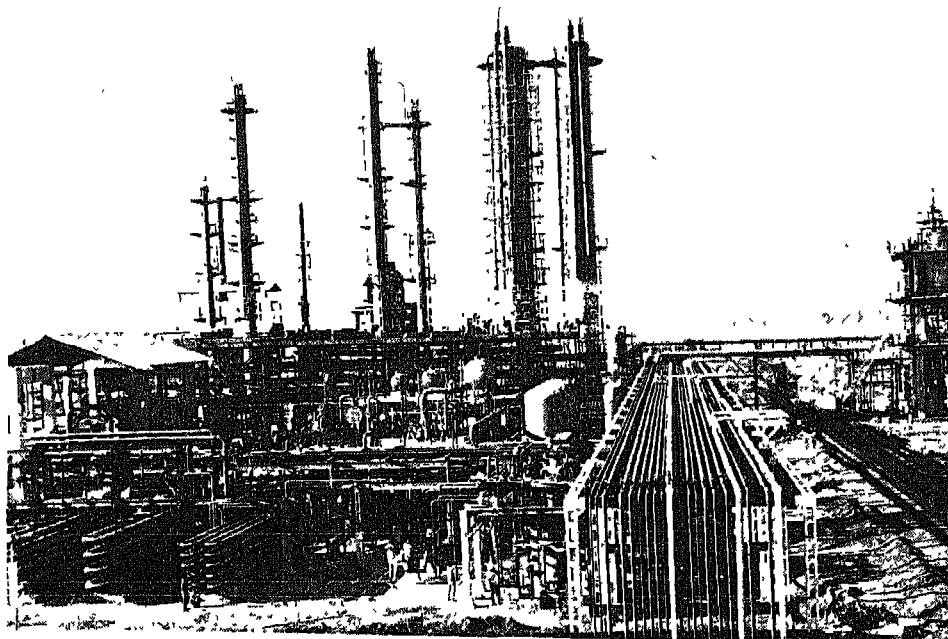


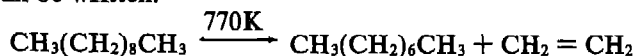
Photo VIII A view of aromatics plants area (xylens plant) of IPCL's Vadodara complex

Courtesy IPCL, Vadodara

### 17.1.5 Cracking and Reforming

Of the various products obtained in straight run refining, the most important are petrol, diesel and kerosene. The demand for these products is more than what is obtained from the above method. Therefore, techniques have been developed to increase the availability of these fractions by either cracking or reforming. In cracking, a larger molecule is broken down into smaller molecules. Reforming, which is used primarily to improve the quality of gasoline, converts straight chain alkanes into arenes.

**Cracking:** Pyrolysis of fuel oil and lubricating oil at about 770K results in random cleavage of carbon-carbon bonds. This process, which is important in petroleum refining, is known as CRACKING. Using decane as an example, the following equation can be written:



In the equation given above, octane and ethene have been shown as products. However, as the C-C cleavage in the first step is random, cracking of decane can produce other hydrocarbons like heptane, hexane, pentane, butane, propene, butene, pentene, hexene, etc. Thermal cracking is difficult to control and gives rise to

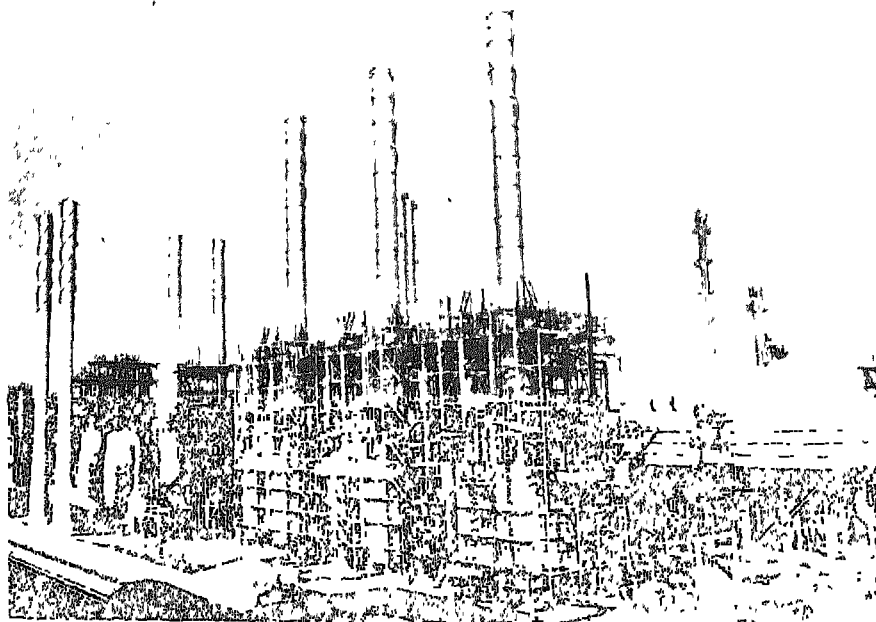
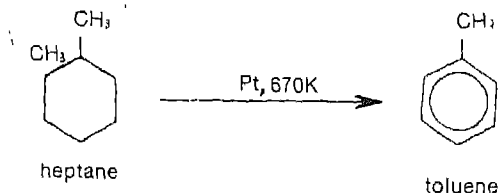


Photo IX STR heater section (heart of the Naphtha Cracker Plant of IPCL, Vadodara)

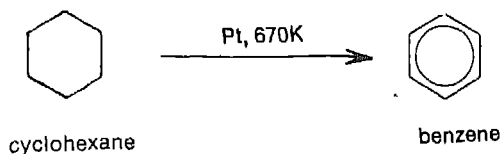
Courtesy-IPCL, Vadodara

complex product mixtures. Nowadays, catalytic cracking, using silica and alumina as catalysts at lower temperatures (600-650K), is more common. Besides being a source of gasoline, cracking is the manufacturing method for industrially important alkenes like ethene, propene and butene.

**Reforming.** REFORMING is the process for obtaining aromatic hydrocarbons from cyclic and acyclic alkanes. In the early days, aromatic hydrocarbons, the bulk of these came from coal tar. But now they are derived from petroleum, mainly by the process of reforming. In this process, cyclic and acyclic alkanes containing six to eight carbon atoms are heated at 600-700 K in the presence of platinum, platinum or nickel as catalyst. Platinum seems to be the best catalyst and so the process is sometimes called PLATFORMING. Following are two examples of platforming. Besides improving the quality of gasoline, arenes like benzene, toluene and xylenes are used to manufacture many other organic chemicals.



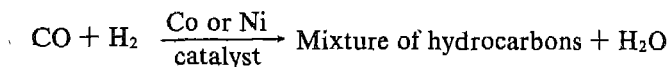




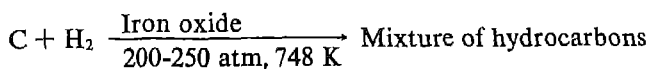
### 17.1.6 Aliphatic Hydrocarbons from Coal

Fuels resembling those obtained from petroleum can also be produced from coal by two methods, namely the Fischer-Tropsch process and the Bergius process. During World War II, Germany, whose petroleum supplies were cut off, produced considerable amounts of fuel from coal by the above processes. The uncertainties in the world oil market today are generating a renewed interest in these methods, especially in countries rich in coal but poor in oil.

The Fischer-Tropsch process consists of passing a mixture of water gas (CO + H<sub>2</sub>) and excess hydrogen over heated cobalt or nickel as catalyst. A mixture of hydrocarbons is produced and this can be refined as needed in the usual manner.



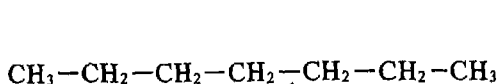
In the Bergius process powdered coal is hydrogenated at 748 K, at 200-250 atmospheres in the presence of iron oxide as catalyst. A mixture of liquid hydrocarbons of good quality gasoline is produced.



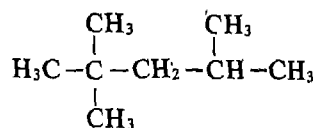
### 17.1.7 Quality of Gasoline—Octane Number

An internal combustion engine gets its power by controlled combustion of vapourised fuel and air. If a low quality fuel is used, the fuel does not burn smoothly. An explosive sound is produced occasionally. It is known as KNOCKING. This greatly reduces the power of the engine. A fuel which produces minimum knocking is considered as a good quality fuel. The quality of a fuel is indicated in terms of its OCTANE NUMBER. An arbitrary scale of octane number has been set up, with n-heptane and 2,2,4-trimethylpentane (iso-octane) as reference compounds. Iso-octane was at one time considered an ideal fuel and was given an octane number 100. Heptane knocks very badly and was given an octane number zero. The octane number of any fuel is defined as the percent of iso-octane in a mixture of iso-octane and heptane which corresponds to the fuel under test in knocking. Therefore, the antiknock property of a fuel increases with the increase of octane number. Branched chain alkanes, alkenes and aromatic hydrocarbons have high octane numbers. These compounds with higher octane numbers are added to straight-run gasoline to raise

its octane number. These compounds are prepared by catalytic cracking and catalytic reforming



n-Heptane



2,2,4-Trimethylpentane

### 17.1.8 Gasoline Additives

The octane number of gasoline is also greatly improved by the addition of tetraethyllead,  $\text{Pb}(\text{C}_2\text{H}_5)_4$ . Such compounds which improve the octane number of a fuel are termed as antiknock compounds. Gasoline containing tetraethyllead is called leaded gasoline or ethyl gasoline.

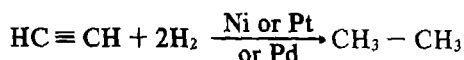
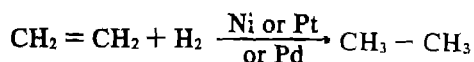
A gasoline-engine discharges various substances into the atmosphere. These are carbon dioxide, water, carbon monoxide, nitrogen oxides, unburnt hydrocarbons from leaded gasoline and certain compounds of lead. Some of these substances are highly poisonous. Their emission into the atmosphere, with the increasing use of automobiles, is a serious pollution problem. Certain devices are now being used to oxidise the unburnt hydrocarbons and carbon monoxide to carbon dioxide and decompose nitrogen oxides into nitrogen and oxygen. The addition of tetraethyllead in gasoline can be avoided by increasing the octane number of fuel by adding certain aromatics and branched chain hydrocarbons.

## 17.2 LABORATORY PREPARATION OF ALKANES

As we have seen earlier, petroleum is the most important large scale source for numerous hydrocarbons including alkanes. However, many alkanes are not available from petroleum or are needed in small quantities for use in the laboratory. Some of the laboratory methods of preparation of alkanes are given in the next few sections.

### 17.2.1 From Unsaturated Hydrocarbons

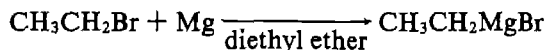
The process of addition of hydrogen to an unsaturated compound in the presence of a catalyst is known as hydrogenation or reduction. Alkenes and alkynes are converted to alkanes by this process. Hydrogenation reactions are involved in the manufacture of *vanaspati* from edible vegetable oils.



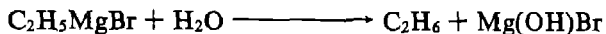
### 17.2.2 From Alkyl Halides

Alkyl halides can be converted to alkanes by any one of the following methods

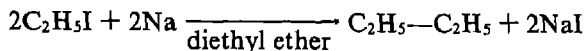
*Using Grignard Reagents:* Alkyl halides, especially chlorides, bromides, and iodides, react with magnesium metal in ethoxyethane (diethyl ether) to form alkyl-magnesium halides. Alkylmagnesium halides are also known as Grignard reagents in honour of Victor Grignard who discovered these versatile reagents and was awarded the Nobel Prize in Chemistry in 1912 for this work.



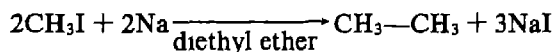
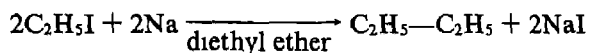
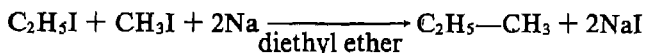
As the carbon atom is relatively more negative than magnesium, it readily reacts with proton donors like water and acids to give an alkane.



*Wurtz Reaction:* When an alkyl halide (usually bromide or iodide) is treated with sodium in diethyl ether a symmetrical alkane containing twice the number of carbon atoms present in the alkyl group is obtained

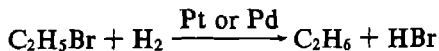
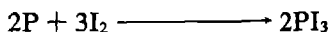
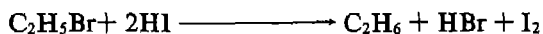


This method gives an alkane with even number of carbons. If two different alkyl halides are reacted for preparing an alkane with odd number of carbons, a mixture of three products is obtained as illustrated:



Therefore, the Wurtz reaction is not useful to prepare alkanes with odd number of carbons as a mixture of hydrocarbons is obtained.

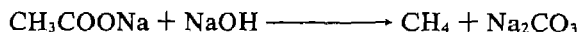
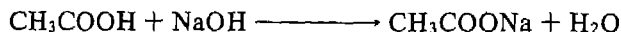
*Reduction of alkyl halides:* Alkyl halides (again mainly bromides and iodides) can be converted to alkanes by reducing them with either red phosphorus and hydroiodic acid or hydrogen in the presence of a catalyst. As the iodine produced in the reaction can react further with the alkane, it is removed by reaction with red phosphorus.



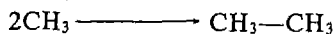
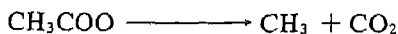
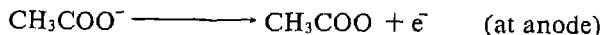
### 17.2.3 From Carboxylic Acids

Two general methods are available for the preparation of alkanes from carboxylic acids. They are (i) decarboxylation, and (ii) Kolbe's electrolytic method.

**Decarboxylation:** When a carboxylic acid is heated with soda lime (NaOH and CaO in the ratio 3:1) to about 630 K, it results in the loss of CO<sub>2</sub> (hence decarboxylation) and the formation of an alkane with one less carbon



**Kolbe's electrolytic method:** When the sodium salt of a carboxylic acid is electrolysed, an alkane is obtained at the anode through the following series of reactions



Kolbe's reaction laid the foundation for the development of electro-organic chemistry.

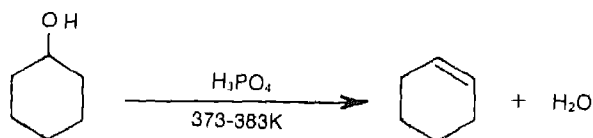
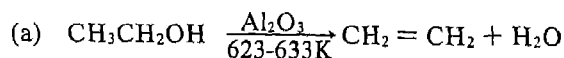
In this method also, like in the Wurtz reaction, an alkane with an even number of carbons is formed. Alkanes with odd numbers of carbons cannot be prepared by this reaction.

## 17.3 LABORATORY PREPARATION OF ALKENES

Alkenes are usually prepared in the laboratory from either alcohols or alkyl halides

### 17.3.1 From Alcohols

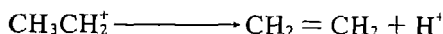
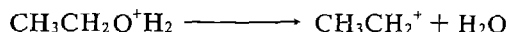
Removal of a molecule of water (dehydration) from an alcohol results in an alkene. The two common methods for effecting dehydration are to heat the alcohol with either alumina or a mineral acid.



The loss of water from an alcohol to give an alkene does not occur in just one step, a series of steps are involved. An understanding of such a series of reaction steps is known as the mechanism of a reaction. Thus, in the dehydration reaction given above, the following steps are involved. First, the acid protonates the alcohol on the most electro-negative atom, namely oxygen. This process is usually reversible. In the second step, the protonated alcohol loses water to give a positively charged species,

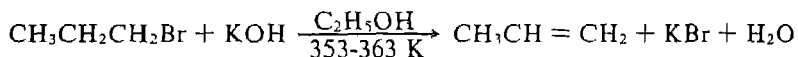


known as a CARBONIUM ION or CARBOCATION. Finally, the carbonium ion loses a proton and forms an alkene.



### 17.3.2 From Alkyl Halides

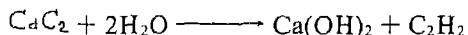
Removal of a molecule of a hydrogen halide from an alkyl halide (usually bromides or iodides and less commonly, chlorides) results in the formation of an alkene. As a molecule of HX is lost, this reaction is also termed as a dehydrohalogenation. This reaction is most commonly done by heating an alkyl halide with alcoholic potassium hydroxide.



Reactions in which a small molecule like  $\text{H}_2\text{O}$  or HX is lost are known as ELIMINATION REACTIONS.

## 17.4 PREPARATION OF ALKYNES IN THE LABORATORY

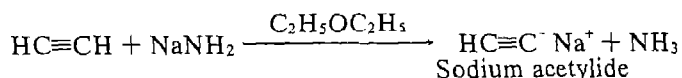
In contrast to alkanes and alkenes, the methods available for the preparation of alkynes are not many. The simplest alkyne, ethyne (acetylene) is obtained by reacting calcium carbide with water. Calcium carbide is manufactured from limestone and coke (see Unit 7 for a brief account of carbides).

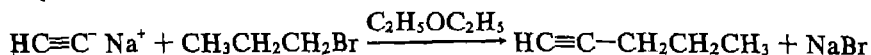


A general method for the preparation of higher alkynes is given below.

### 17.4.1 From Acetylene

Acetylene reacts with sodium amide to form sodium acetylide. The acetylide on treatment with an alkyl halide leads to a homologated acetylene. This reaction is explained in detail towards the end of this Unit.





### 17.5 PHYSICAL PROPERTIES OF ALKANES

Some of the physical properties that we will study in this section are boiling point, melting point, density and solubility. All these properties depend upon the inter-molecular forces between the molecules. These forces are of the van der Waals type (chapter 3) and in turn depend upon the shape and hence the structure of the molecules. Thus, for example, a straight chain molecule has more contact with an adjacent molecule when compared to a branched chain molecule which is more compact and has less contact. Therefore, the van der Waals forces are greater in straight chain molecules than in branched chain molecules.

Among the straight chain alkanes, the first four ( $\text{C}_1$  to  $\text{C}_4$ ) are gases, the next thirteen are liquids ( $\text{C}_5$  to  $\text{C}_{17}$ ) and the higher molecules are solids. All of them are colourless.

#### 17.5.1 Boiling Points

The boiling points of alkanes increase with increase in their molecular mass. Each carbon added to the chain increases the boiling point by about 20-30 K. The difference is greater for the lower homologues than for the higher ones. This regular increase in boiling point with increase in carbon content is due to greater surface area and contact and hence larger van der Waals forces as we go up a homologous series. The same trend is observed for alkenes and alkynes as well.

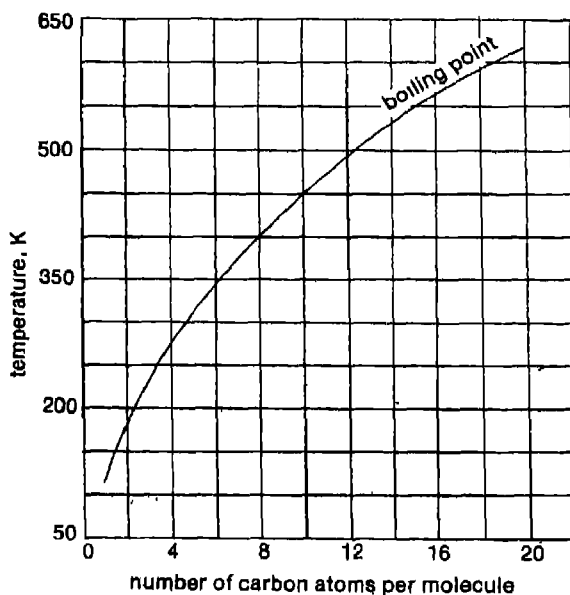


Fig. 17.2 Graph showing variation in boiling points of *n*-alkane with increase in the number of carbon atoms per molecule of the homologous series

Branched compounds have lower boiling points than their straight chain isomers. Thus, in the case of the  $C_5H_{12}$  isomers, the straight chain compound, pentane, boils at 309 K, the single branched isomer, 2-methylbutane, boils at 301 K and the doubly branched, 2,2-dimethylpropane, boils at 282.5 K. This variation can be readily explained. As we go from a straight chain to a single branched to a double branched isomer, the molecular shape becomes more and more compact, thereby resulting in a decrease in the van der Waals forces. Therefore, the boiling points also decrease. All these are illustrated in Fig. 17.2.

### 17.5.2 Melting Points

Variations in the melting points of alkanes are not regular, because these depend on how the molecules are packed in the crystal. However, when melting points of normal alkanes are plotted against the number of carbon atoms in a chain, a sawtooth pattern is found (Fig. 17.3).

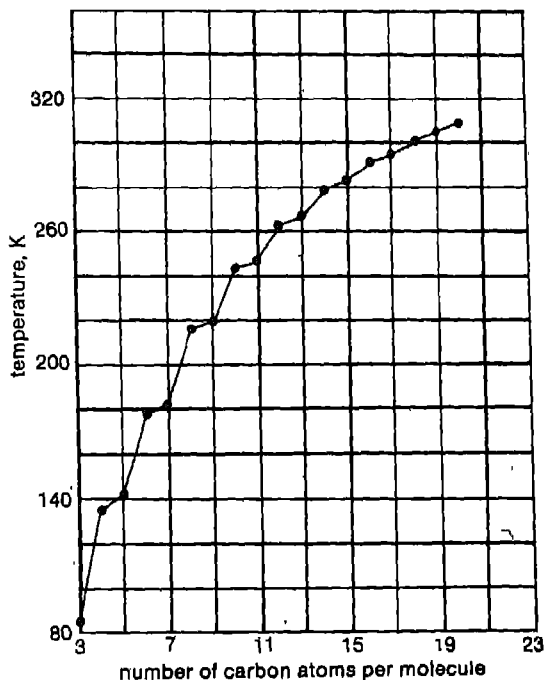


Fig 17.3 Variation in melting points of *n*-alkanes with increase in number of carbon atoms

Molecules with an odd number of carbon atoms have lower melting points than those with an even number of carbon atoms. This implies that molecules with an odd number of carbon atoms are poorly aligned in the crystal compared to molecules

with an even number of carbon atoms. The same kind of alternation effect is found in alkenes and alkynes. This is associated with the shape in space or conformation of the hydrocarbon chains in the crystals in the solid state. Due to  $sp^3$  hybridisation in alkanes, any two bonds of a carbon atom make an angle of about  $109^\circ 28'$  with one another. The most extended form of an unbranched carbon chain is zig-zag and not straight as is commonly written.

Terminal methyl groups of alkanes lie on the same side when the number of carbon atoms is odd, and on opposite sides when the number is even (Fig 17.4)

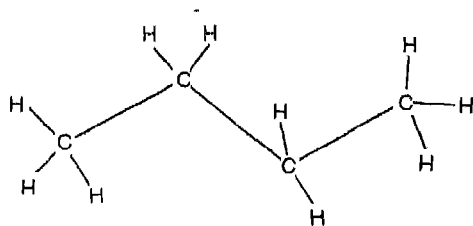


Fig 17.4 Diagrammatic representation of extended form of alkane (butane) containing even number of carbon atoms

Crystalline forms of alkanes are built up of molecules with extended chains. Therefore, the difference in arrangement of the  $CH_3$  group of odd and even carbon compounds appreciably affects the forces of interaction and hence the melting temperature. In the liquid state, where the shapes of the molecules keep changing as a result of collisions, such alternation effect is not observed (see boiling points)

In alkenes, where geometric isomerism is possible, melting points depend on the structure of the molecule. For example, *cis*-2-butene has a lower melting point than *trans*-2-butene. Amongst isomeric dimethylbenzenes (xylenes), the para-isomer has the highest melting point. The effect is most dramatic when we compare the melting points of benzene (278 K) and toluene (178 K), the introduction of a single methyl group into the highly symmetrical benzene molecule causes such a drastic change.

### 17.5.3 Solubility and Density

The solubility behaviour of most compounds is described by the popular statement, 'like dissolves like'. Acyclic compounds which are non-polar are soluble in non-polar or slightly polar solvents such as benzene, ether, carbon tetrachloride, etc., but are insoluble in water and other polar solvents. Alkanes themselves are good non-polar solvents, which dissolve non-polar or slightly polar compounds.

The density of alkanes increases with increase in the size of the molecule but reaches the limiting value at about  $800 \text{ kg m}^{-3}$ . Generally, hydrocarbons are lighter than water.

## 17.6 REACTIONS OF HYDROCARBONS

The reactions of hydrocarbons are directly related to their structures. As we have seen earlier in Unit 16, alkanes are saturated hydrocarbons with only carbon-carbon



single bonds and carbon-hydrogen bonds. Alkenes and alkynes are all unsaturated hydrocarbons. Whereas alkenes have carbon-carbon double bonds, alkynes have carbon-carbon triple bonds. The double and triple bonds comprise a  $\sigma$ -bond and one and two  $\pi$ -bonds, respectively. As a  $\pi$ -bond is weaker than  $\sigma$ -bond, it is also more reactive. Consequently, alkenes and alkynes are more reactive than alkanes. Arenes are also more reactive than alkanes but are not comparable to alkenes and alkynes. This is due to special properties of the benzene structure, which were mentioned in Unit 16. The relative inertness of alkanes have earned them the name 'paraffins' (Latin: little affinity or reactivity).

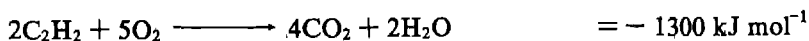
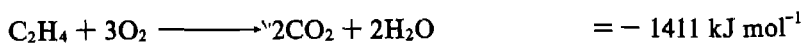
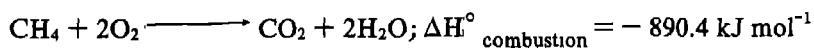
The main reactions of hydrocarbons can be conveniently classified and studied under four heads:-

(1) oxidation (including combustion and fragmentation); (2) addition; (3) substitution and (4) miscellaneous reactions.

### 17.6.1 Oxidation (including Combustion and Fragmentation)

All hydrocarbons undergo oxidation under certain conditions. The more common oxidising agents which react with hydrocarbons are oxygen, potassium permanganate and ozone. We will now discuss the oxidation of hydrocarbons with these three oxidising agents.

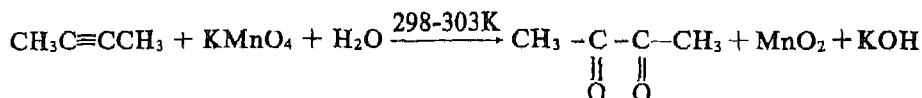
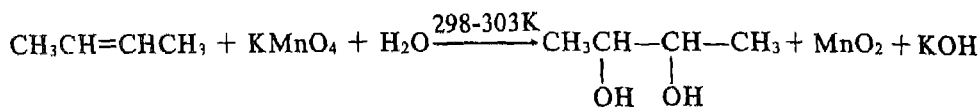
**Complete Oxidation with Oxygen-combustion:** All hydrocarbons are combustible. They burn in air or oxygen producing carbon dioxide and water and liberate heat in the process. Incomplete combustion results in the formation of carbon monoxide and unburnt carbon (carbon black and soot). In general, alkanes undergo complete combustion readily (with a blue flame), but alkenes, alkynes and arenes do not get oxidised completely and burn with a luminous, yellow, sooty flame. The colour of the flame, when an organic compound is burnt, was for long used as a qualitative tool in organic chemistry to distinguish between saturated and unsaturated compounds. Hydrocarbons find extensive use as fuels like liquified petroleum gas (LPG), petrol, kerosene and diesel. This is due to the strongly exothermic nature of the combustion reaction



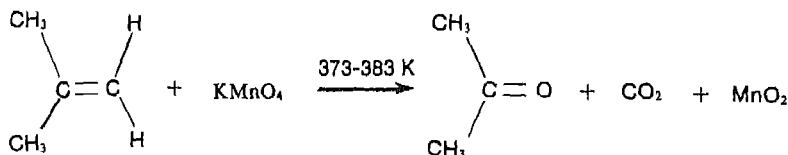
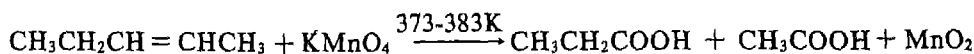
**Oxidation with Potassium Permanganate:** Combustion of hydrocarbon in air or oxygen is useful for realising their calorific value only. However, as we have seen earlier in this chapter, hydrocarbons are the parent compounds for other organic compounds and are also abundantly available. For transforming hydrocarbons into other useful organic compounds, controlled oxidation is desirable. Of the many methods available for this purpose, we will study the reactions of hydrocarbons with potassium permanganate and ozone.

Alkanes, due to their structural features (only  $\sigma$ -bonds and no  $\pi$ -bonds) do not react with potassium permanganate. Unsaturated compounds like alkenes and

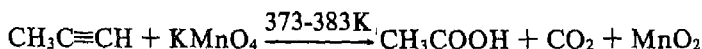
alkynes react quite readily. The products obtained depend upon the reaction conditions, with *cold, dilute* potassium permanganate solution, alkenes and alkynes react as shown to give 1,2-diols (1,2-glycols) and 1,2-diketones respectively. As potassium permanganate is reduced to manganese dioxide in the process, the purple



colour is discharged. This reaction is used in qualitative organic analysis to test for the presence of an unsaturated hydrocarbon. Under more severe conditions, the double bond is cleaved and the final products are carboxylic acids, ketones and carbon dioxide depending upon the nature of the double bond as illustrated below.

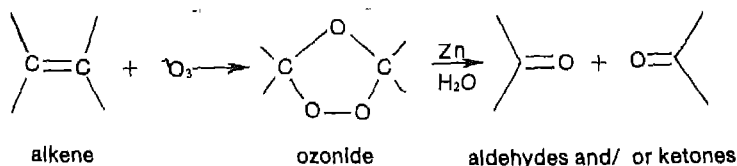


With alkynes also a similar reaction occurs.



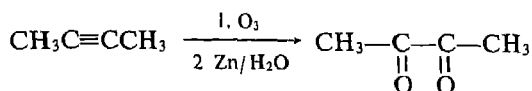
If the products of these cleavage reactions can be characterised, then the structure of the starting alkene or alkyne can be determined, as the position of cleavage corresponds to the position of the double or triple bond.

**Oxidation with Ozone:** Alkenes are oxidised by ozone to ozonides. Ozonides are unstable and explosive compounds. They are not isolated but are reduced with zinc and water. The products are aldehydes or ketones, resulting from the cleavage of the carbon-carbon double bond. The process is known as ozonolysis and is shown below.



If a hydrogen is attached to the carbon forming the double bond, an aldehyde results, otherwise, ketones are formed. Analysis of the product of ozonolysis is

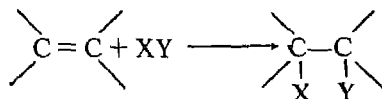
helpful in locating the position of the double bond and was used extensively for structure elucidation in the past. Alkynes give diketones on ozonolysis



The cleavage reactions of alkenes with potassium permanganate and ozone offer methods for the fragmentation of hydrocarbons

### 17.6.2 Addition Reactions

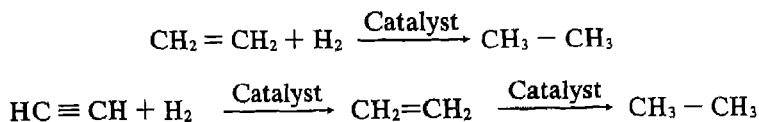
Addition reactions are those in which one reacting molecule adds on to the multiple bond of the other reacting molecule. In the process, the  $\pi$ -bond of the multiple bond is broken and two new  $\sigma$ -bonds are formed. Thus, for example, in the case of an alkene, we have



By the very definition of an addition reaction, it is immediately obvious that alkanes cannot participate in an addition reaction. The unsaturated hydrocarbons—alkenes, alkynes and arenes all undergo addition reactions. For purposes of our study, addition reactions can be broadly classified as follows.

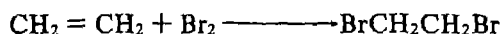
- Addition of hydrogen
- Addition of halogens
- Addition of unsymmetrical reagents
- Addition to arenes
- Polymerisation

**Addition of Hydrogen:** Alkenes and alkynes react readily with hydrogen in the presence of finely divided nickel, platinum or palladium as catalysts. The process is known as hydrogenation

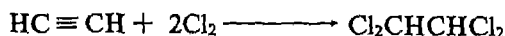
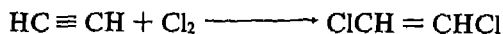


In the case of alkynes, the intermediate alkenes can be isolated by choosing the right reaction conditions. Hydrogenation is used in the manufacture of *vanaspathi* from vegetable oils. Many vegetable oils contain double bonds and become rancid on prolonged storage due to reaction at the double bonds. Hydrogenation converts the double bonds into saturated bonds and thereby prevents rancidity.

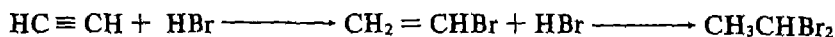
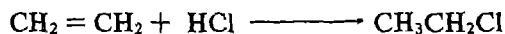
**Addition of Halogens:** Alkenes and alkynes react readily with halogens, especially chlorine and bromine, producing a di- or tetrahalogen derivative. Thus, ethylene reacts with bromine to give 1,2-dibromoethane.



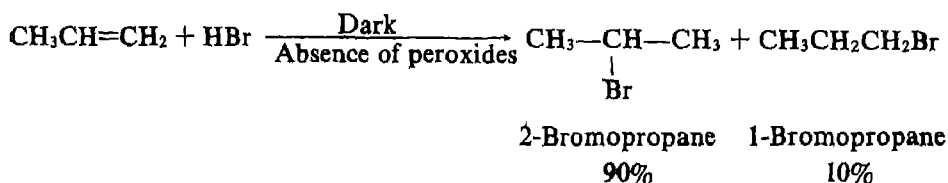
In alkynes, due to the presence of two  $\pi$ -bonds each molecule of the alkyne can react with two molecules of the halogen. As illustrated for acetylene, the addition of halogen (chlorine) can be controlled to give 1,2-dichloroethene or 1,1,2,2-tetrachloroethane.



*Addition of Unsymmetrical Reagents:* Most of the addition reactions of alkenes and alkynes are those with unsymmetrical reagents like HCl, HBr and H<sub>2</sub>O. When such reagents react with alkenes and alkynes, one part of the molecule bonds to one carbon atom and the other part to the second carbon atom

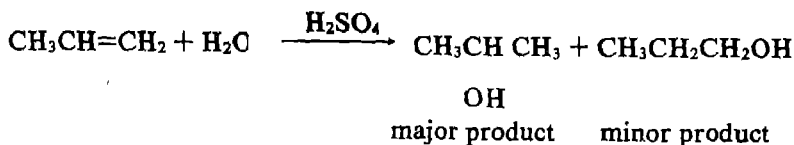


However, if the alkene and the reagent are both unsymmetric then two products are possible, as illustrated for the reaction between propene and HBr, in the dark and in the absence of peroxides. Experimentally, under these conditions, the major product is 2-bromopropane and the minor product is 1-bromopropane. After



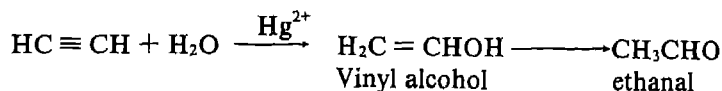
the study of the reaction of hydrogen halides with a variety of alkenes, the Russian chemist, Markownikoff, postulated in 1869 that, "In the addition of HX molecules to an unsymmetrical alkene, the hydrogen goes to the carbon atom which already has a larger number of hydrogen atoms attached to it". This is today known as Markownikoff's rule and can be used to predict the major product when a molecule of HX adds to an unsymmetrical alkene.

Water also adds to alkenes and alkynes in the presence of mineral acids and mercuric ions as catalyst, respectively. In this case also, Markownikoff's rule is obeyed and propene gives 2-propanol and not 1-propanol as the major product. The

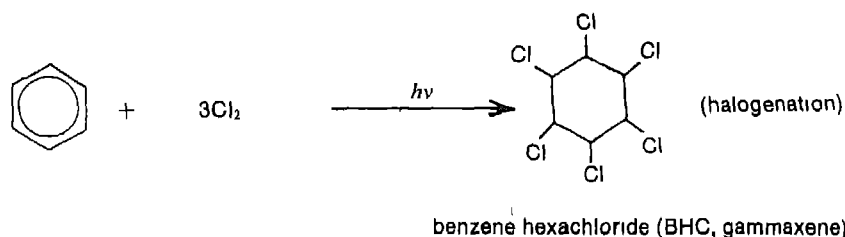
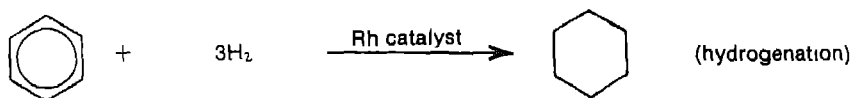


reaction of an alkene with water to give an alcohol is known as hydration and is an industrially important method for the manufacture of alcohols.

Alkynes undergo hydration in the presence of mercuric ions as a catalyst. The products are carbonyl compounds. In the case of ethyne (acetylene), ethanal (acetaldehyde) is produced. The initially formed vinyl alcohol is unstable and rearranges to the more stable ethanal.



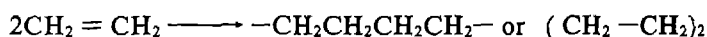
**Addition to Arenes:** Benzene and its homologues undergo some addition reactions characteristic of alkenes and alkynes, but under more drastic conditions (like higher temperature and pressure) This is due to the extra stability of the delocalised  $\pi$ -electrons in benzene. Two such addition reactions are hydrogenation and halogenation.



BHC is used as an insecticide and is manufactured by many companies in India.

**Polymerisation:** Polymerisation is a process in which a large number of simple molecules combine to form a large molecule, known as a macromolecule or a polymer. The simple molecules are known as monomers. Polymers have helped to revolutionise our everyday living. The polymers are used in plastics, textile, rubber and many other industries.

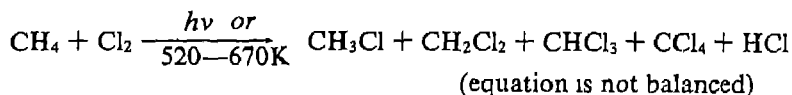
Alkenes undergo polymerisation in the presence of catalysts. In this process, one alkene molecule links to another molecule as represented by the following reaction of ethene



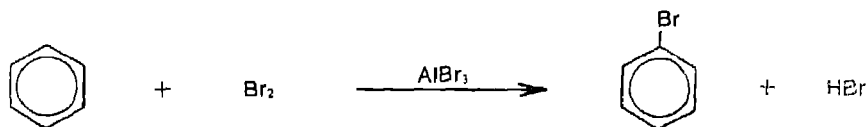
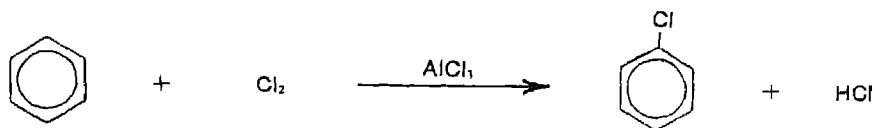
In the case of 'n' number of molecules of ethene, the reaction is represented as follows:



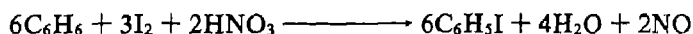
atoms, the reaction is one of substitution. It is also known as halogenation or more specifically chlorination, as a chlorine atom is introduced.



*Substitution in Arenes:* Chlorine or bromine reacts with benzene in the presence of Lewis acids like ferric or aluminum salts of the corresponding halogen which act as catalysts.

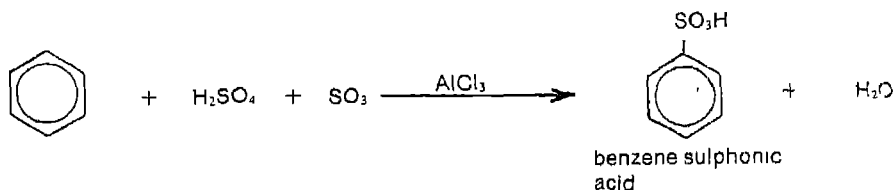


Iodobenzene is obtained by heating benzene with iodine and nitric acid

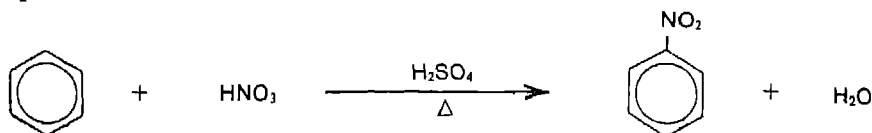


Fluorination is very vigorous in the case of arenes and is rarely used to prepare fluoroarenes.

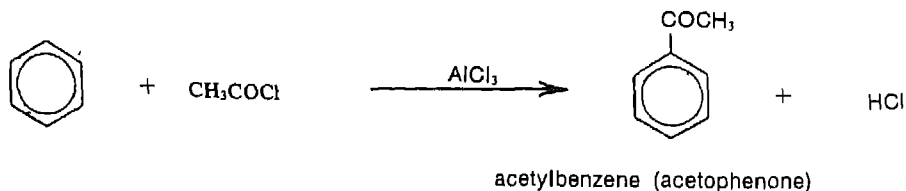
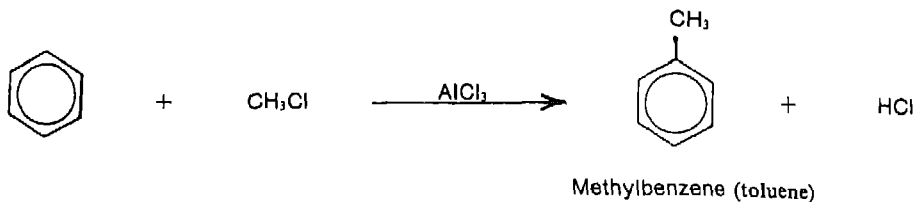
The replacement of hydrogen atom of benzene by a sulphonic acid group ( $-\text{SO}_3\text{H}$ ) is known as sulphonation. The reaction is carried out by treating an arene with concentrated sulphuric acid containing dissolved sulphur trioxide or with chlorosulphonic acid.



A nitro group can be introduced into a benzene ring using a mixture of nitric and sulphuric acids.



**Friedel-Crafts Reaction:** On treatment with an alkyl halide or a carboxylic acid halide (acyl halide) in the presence of anhydrous aluminium chloride as catalyst, benzene forms an alkyl or an acylbenzene.



Toluene is a homologue of benzene and acetophenone is an aromatic ketone.

#### 17.6.4 Miscellaneous Reactions

In this category, we will consider two reactions:

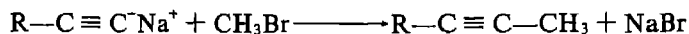
- (i) fragmentation of alkanes, and
- (ii) acidic character of alkynes.

i) **Fragmentation of Alkanes:** When alkanes are heated to high temperatures (about 700-800K) or to a slightly lower temperature in the presence of alumina or silica catalysts, they break down to give smaller alkanes and alkenes. This process is known as fragmentation or cracking and is discussed earlier in this Unit.

ii) **Acidic Character of Alkynes:** Alkynes react with strong bases like  $\text{NaNH}_2$  to form acetylides. The acetylenic hydrogen atom is removed as a proton by the strong base leading to the formation of a stable carbanion.



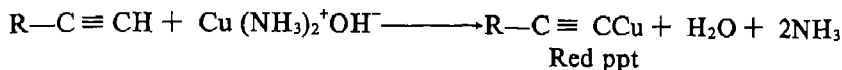
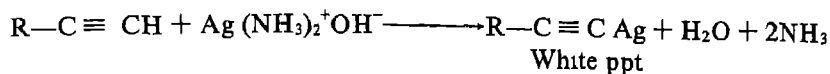
Acetylides react with alkyl halides to produce acetylene homologues.



The acetylenic hydrogen of alkynes can also be replaced by copper (I) or silver ions.

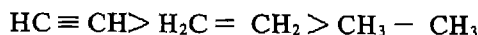


in ammoniacal medium



The reactions show that alkynes are acidic in nature. Alkanes and alkenes do not give these reactions

The acidic character of alkynes may be explained in terms of the character of the  $sp$  hybridised orbital. An electron in an  $s$  orbital is more tightly held than in a  $p$  orbital because the  $s$ -electrons are closer to the nucleus. Since there is more  $s$ -character in  $sp$  orbitals compared to  $sp^2$  and  $sp^3$  orbitals, the electrons in  $sp$  orbitals are held more strongly by the nucleus than  $sp^2$  and  $sp^3$  electrons. In other words, the  $sp$  hybridised carbon is more electronegative than  $sp^2$  and  $sp^3$  hybridised carbon atoms. Due to this, the hydrogen of acetylenic carbon develops a more positive charge and is acidic in character. The acidic character of hydrocarbons decreases in the following order.



Compared to organic acids like ethanoic acid (acetic acid), hydrocarbons are very weakly acidic. Ethyne (acetylene) is about  $10^{20}$  times less acidic than ethanoic acid and ethane, about  $10^{40}$  times less acidic.

## EXERCISES

- 17.1 What is straight-run gasoline? Describe the principle of obtaining straight-run gasoline from petroleum
- 17.2 Explain the term 'knocking' What is the relationship between the structure of a hydrocarbon and knocking?
- 17.3 (i) Describe a scale for measuring the quality of gasoline  
(ii) A sample of gasoline produces the same knocking as a mixture containing 35% n-heptane and 65% iso-octane What is the octane number of the sample?
- 17.4 Explain the following processes  
(i) cracking  
(ii) reforming
- 17.5 Describe different methods to improve the quality of a fuel used in a gasoline engine
- 17.6 Explain the following with examples  
(i) Wurtz Reaction  
(ii) Kolbe's Electrolytic method  
(iii) Hydrogenation  
(iv) Dehydration.

17.7 How are the following conversions carried out?

- ✓ (i) propene to propane
- (ii) acetylene to ethane
- (iii) ethyl alcohol to ethene
- ✓ (iv) sodium acetate to methane
- ✓ (v) propene to 2-bromopropane
- (vi) methane to tetrachloromethane
- ✓ (vii) benzene to nitrobenzene

17.8 Write the equations for the preparation of propyne from acetylene.

17.9 What happens when

- (i) 1-bromopropane is heated with alcoholic caustic potash
- (ii) 2-propanol is heated with alumina at 630 K
- (iii) benzene is treated with a mixture of concentrated sulphuric and nitric acids
- (iv) ethene is treated with an alkaline potassium permanganate solution (cold)
- (v) benzene is treated with bromine in the presence of aluminium bromide as catalyst

17.10 What is a Grignard reagent? How is propane prepared from a Grignard reagent?

17.11 Write short notes on.

- (i) Friedel Crafts reaction
- (ii) Addition reaction
- (iii) Markownikoff's rule.

17.12 Explain the term 'polymerisation' with two examples

17.13 Give reasons for the following

- (i) The boiling points of hydrocarbons decrease with increase in branching
- (ii) Unsaturated compounds undergo addition reactions
- (iii) Acetylene is acidic in character.

17.14 Describe a method to distinguish between ethane, ethene and ethyne.

## UNIT 18

# PURIFICATION AND CHARACTERISATION OF ORGANIC COMPOUNDS

*Chemists are obsessed with purity.*

### OBJECTIVES

In this Unit, we shall learn

- \* the principles involved in the different methods of purification like crystallisation, sublimation, distillation, extraction and chromatography;
- \* the application of the above principles for the purification of some simple mixtures,
- \* the chemical reactions involved in the qualitative analysis of organic compounds using the sodium fusion test;
- \* the different methods of quantitative analysis to determine the percentage composition of different elements in organic compounds;
- \* calculation of empirical and molecular formulae and molecular masses of organic compounds by different methods.

THE STRUCTURAL FORMULA of an organic compound isolated from a natural source or prepared in the laboratory, can be determined by following a systematic procedure. The different steps employed in the study of organic compounds are. (a) purification, (b) qualitative analysis, (c) quantitative analysis, (d) molecular mass determination, (e) calculation of the empirical and molecular formulae, and (f) determination of structure by one or more of several methods including chemical synthesis. In this Unit, we shall deal with some of the methods commonly employed for the purification and characterisation of organic compounds.

## 18.1. PURIFICATION

Before investigating the structure and properties of an organic compound, it is most essential to obtain it in the pure form. Methods of separating organic compounds from one another and purifying them depend on the differences in their physical properties. The common techniques used are: (a) crystallisation, (b) sublimation, (c) distillation, (d) differential extraction, and (e) chromatography.

The melting point, the boiling point and the refractive index are generally used as the criteria of purity of an organic compound. This is because each pure compound possesses a distinct set of physical properties which differentiate it from other compounds. In recent years, more sophisticated methods are also employed to check purity of compounds, the methods include spectroscopic techniques and different forms of chromatography.

### 18.1.1 Crystallisation

This is an important procedure for purifying solids wherein impurities of differing solubility are removed. Briefly, the method consists of dissolving the solid in a solvent in which it is sparingly soluble at room temperature but appreciably soluble at higher temperatures. This is achieved by heating. Once the bulk of the solid has dissolved, any insoluble impurities present are removed by filtration. On cooling, the pure solid crystallises out. Frequently, to enhance the recovery of the solid, the solution is either concentrated by partial evaporation of the solvent or diluted with a solvent in which the substance is less soluble. The crystals are separated by filtration and then dried.

Let us take the case of sugar containing an impurity of common salt. This can be purified by treating the mixture with ethanol around 348 K. The sugar will dissolve whereas common salt remains insoluble. The filtrate on concentration and cooling will yield pure crystals of sugar. Choice of the solvent is very crucial in such operations. Had water been taken as the solvent in the above case, purification of sugar would not have been possible, because both sugar and common salt are readily soluble in water.

Benzoic acid mixed with naphthalene can be purified by treating the mixture with hot water. Benzoic acid dissolves while naphthalene remains insoluble. The hot solution is filtered and cooled. Pure benzoic acid crystallises out and is separated by filtration. Again we see the importance of the choice of a suitable solvent. If benzene had been taken as a solvent in the above case, purification of benzoic acid

would not have been possible, because both naphthalene and benzoic acid are quite soluble in benzene.

In case the difference in solubility of two substances in solvent is not very marked, fractional crystallisation, involving a series of repeated crystallisations is carried out.

### 18.1.2 Sublimation

This is a method of limited application and is used to purify those solids which sublime readily and contain non-volatile impurities. Certain substances like naphthalene, benzoic acid and camphor on heating are converted to vapours without passing through the intervening liquid state. The vapours on cooling yield crystals of the pure solid compounds. This process is called sublimation.

### 18.1.3 Distillation

This is an important method for purifying liquids and is based on differences in boiling points. Simple distillation involves the conversion of a liquid into vapour by

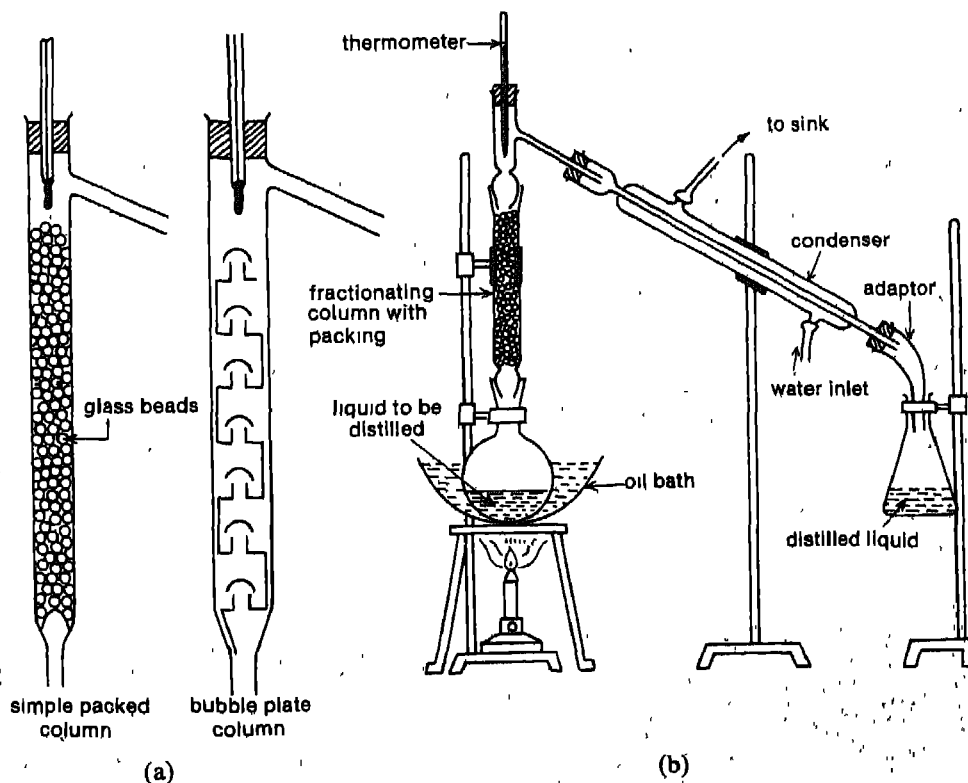


Fig. 18.1 (a) Fractionating columns, (b) Assembly for fractional distillation

heating and then condensation of the vapour into another flask. For example, distillation can be used to separate ether (boiling at 308 K) or hexane (boiling at 342 K) from other liquids boiling above 370 K (e.g. toluene boiling at 383 K). Distillation is also helpful in separating the non-volatile impurities from liquids.

As we have seen earlier if the boiling points of the liquids to be separated are close to each other, fractional distillation is carried out by using a fractionating column (Fig 18.1). Several types of columns have been used but the basic principle is the same; a fractionating column increases the cooling surface and the vapours go up from the distillation flask through the column. The higher boiling liquids are condensed in the lower portions of the column. As the lower portion of the column is hotter than the upper portion, the more volatile components will volatilise and condense in the upper, cooler portion of the column. This amounts to repeated distillation\*.

High boiling liquids as well as liquids which decompose at or below their normal boiling points are generally distilled at lower temperatures under reduced pressure (Fig 18.2). With an ordinary water pump, a pressure of 10-20 mm Hg can be obtained and under these conditions boiling points are reduced by about 100 degrees. Lower pressures (0.1 mm Hg) may be obtained with better vacuum pumps.

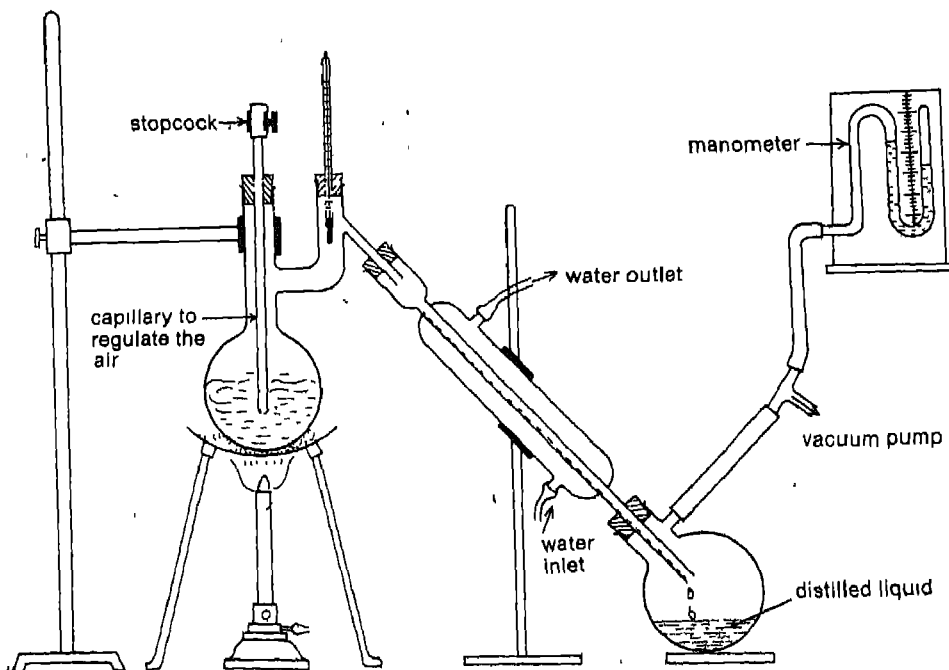


Fig. 18.2 Apparatus for distillation under reduced pressure

\* An industrial application of fractional distillation is the separation of petroleum into various useful fractions about which we have learnt in Unit 17

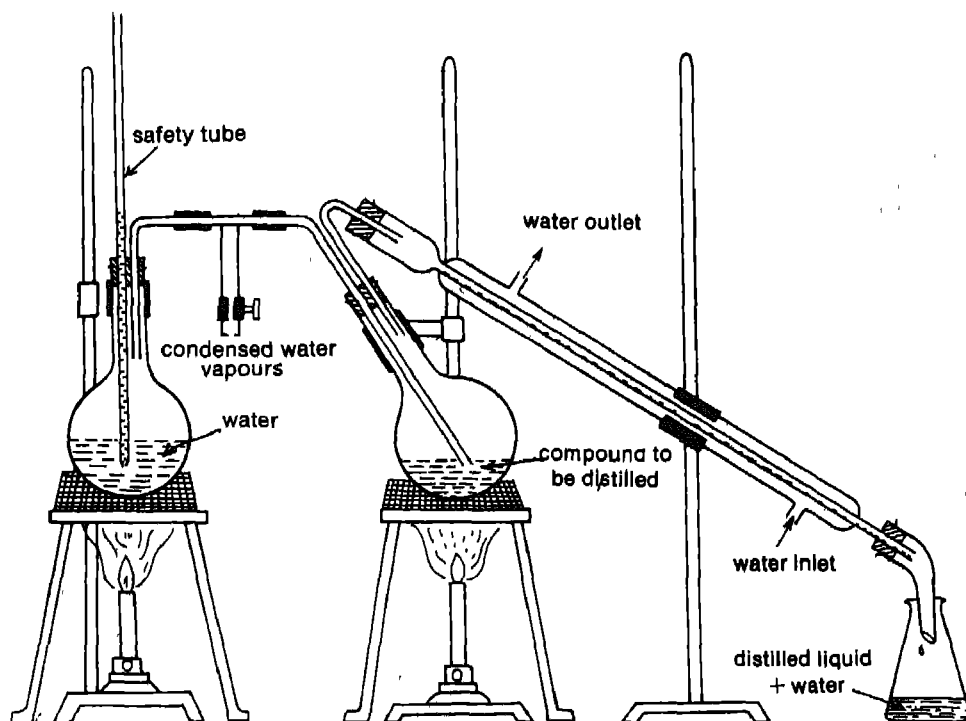


Fig. 18.3 Apparatus for steam distillation

It is often convenient to separate organic compounds from non-volatile organic or inorganic impurities by distillation with steam. This is applicable to only those compounds which are steam volatile and are sparingly soluble in water (e.g., aniline,  $\text{C}_6\text{H}_5\text{NH}_2$ ). Steam distillation can be carried out by passing steam through a heated flask containing the liquid to be distilled (Fig. 18.3). The mixture of steam and the volatile organic compounds (that distils out) is later condensed and the components separated from each other. We know that a liquid boils when its vapour pressure becomes equal to the atmospheric pressure (Unit 3). In steam distillation, water and the organic substance vapourise together and their vapour pressures together equal the atmospheric pressure.

Vapour pressure of organic substance + vapour pressure of water = atmospheric pressure.

Since the vapour pressure of the organic substance has to be lower than atmospheric pressure as per the above equation, the organic substance vapourises at lower temperatures.

The proportion of the organic substance that distils over with steam is related to the vapour pressures as well as molecular masses by the following equation:

$$\frac{W_1}{W_2} = \frac{P_1 M_1}{P_2 M_2}$$

Where W is the mass, P the vapour pressure and M the molecular mass with the subscripts 1 and 2 standing for water and the organic substance respectively

#### 18.1.4 Differential Extraction

When an organic compound is present in aqueous solution, it can be recovered by shaking it with a suitable organic solvent (the compound must have to be more soluble in the organic solvent than in water). The organic solvent should be immiscible with water so that the organic and water layers can be easily separated. The solvent on evaporation leaves behind the recovered substance. This method is normally applicable to non-volatile organic compounds. For example, benzoic acid can be extracted from water solution using benzene (Fig. 18.4).

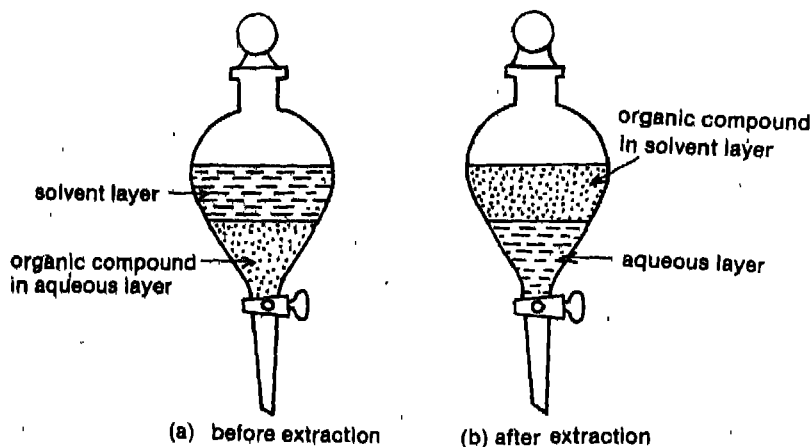


Fig. 18.4 Differential extraction (extraction with solvent lighter than water)

#### 18.1.5 Chromatography

This method is based on the differential adsorption of the various components in a mixture on a suitable adsorbent. It is an extremely valuable method for the separation, isolation, purification and identification of the constituents of a mixture and is based on the general principle of phase distribution.

The simplest chromatographic method is column chromatography. Here, a suitable adsorbent like alumina ( $\text{Al}_2\text{O}_3$ ) is packed in a column and this constitutes the stationary phase. The mixture to be separated is taken in suitable solvent and the solution poured on the top of the column of the adsorbent. The components are then eluted out by a suitable solvent (which acts as a mobile phase). The weakly adsorbed component will be eluted more rapidly than a more strongly adsorbed



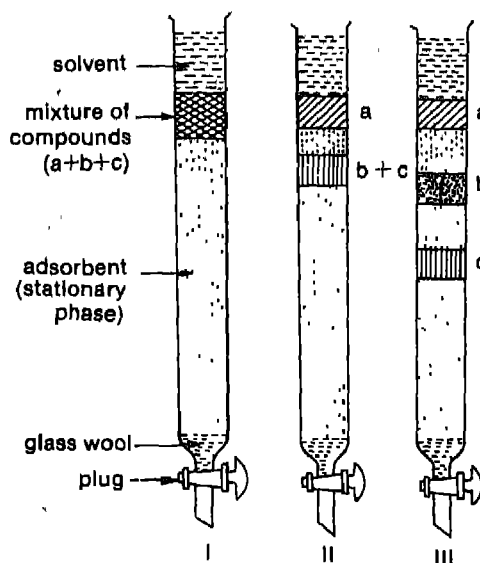


Fig. 18.5 Diagrammatic representation of column chromatography [ I, II and III show the progressive separation of components a,b and c of a mixture with a solvent (eluent)]

component. Such a progressive separation of a mixture is diagrammatically shown in Fig.18.5 We may see separate bands in the column formed by different compounds in the mixture, if they are coloured

Some of the common forms of chromatography are given in the Table 18.1.

## 18.2 QUALITATIVE ANALYSIS

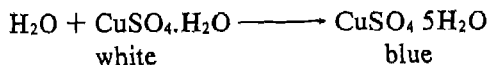
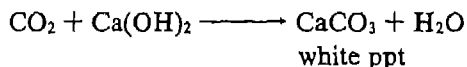
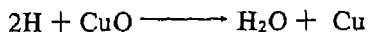
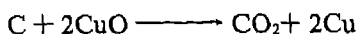
Analysis of an organic compound first involves the detection of elements The elements commonly present in organic compounds are carbon, hydrogen, oxygen,

TABLE 18.1

Common Forms of Chromatography

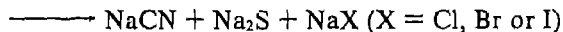
Type of chromatography	Mobile/Stationary phase	Uses
Column	Liquid/Solid	Preparative (large) scale separations
High performance liquid (HPLC)	Liquid/Solid	Qualitative and quantitative analysis; preparative scale separation
Thin layer (TLC)	Liquid/Solid	Qualitative analysis
Gas liquid (GLC)	Gas/Liquid	Qualitative and quantitative analysis
Paper	Liquid/Liquid	Qualitative and quantitative analysis of polar organic and inorganic compounds

nitrogen, halogens, sulphur and phosphorus Carbon and hydrogen are normally detected by strongly heating a mixture of the organic compound and cupric oxide. The carbon present is oxidised to carbon dioxide (tested by lime water) and hydrogen to water (tested by anhydrous copper sulphate).

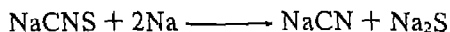
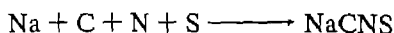


Nitrogen, sulphur and halogens in the organic compounds are detected by LASSAIGNE'S TEST. These elements are covalently bonded in organic compounds and have to be first converted into the ionic forms. This is done by the fusion of an organic compound with sodium metal. In this way sodium cyanide, sodium sulphide and sodium halides are formed.

Organic compound containing C, H, O, N, S, Halogens + sodium



If nitrogen and sulphur both are present in the organic compound, they may give sodium thiocyanate (NaSCN), which in the presence of excess sodium, forms sodium cyanide and sodium sulphide.



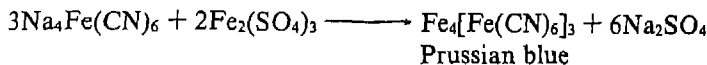
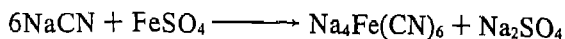
A systematic analysis of the products obtained from the sodium fusion test enables us to identify the elements present in the organic compound of interest.

A small piece of sodium is heated in a small, dry test tube till the sodium starts to vapourise. The tube is removed from the flame, the organic compound (about 50-60 mg) added and the tube heated strongly for 2-3 minutes. After cooling, the tube is carefully broken in a mortar containing water, when the sodium salts formed in the above reactions (i.e. NaCN, Na<sub>2</sub>S, NaX or NaSCN) dissolve. Excess of sodium reacts with water to give sodium hydroxide. This alkaline solution is called Lassaigne's solution. The solution is first filtered to remove insoluble materials and the clear filtrate is used for further testing.

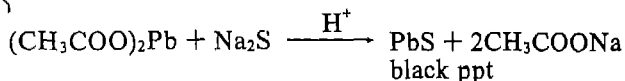
**Test for Nitrogen.** The filtrate from the sodium fusion test is heated to boiling with ferrous sulphate crystals and then acidified with dilute sulphuric acid. If nitrogen is present, a blue precipitate or blue colour is observed.

The reactions involved in this test are as follows: On reaction with ferrous sulphate gives sodium ferrocyanide. On heating, some of the ferrous

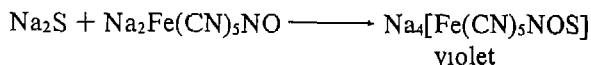
salt is oxidised to the ferric salt and this reacts with sodium ferrocyanide to form ferric ferrocyanide



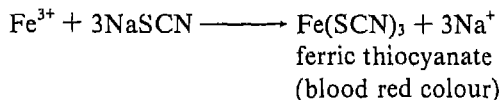
*Test for Sulphur:* (a) Lassaigne's solution is acidified with acetic acid and lead acetate solution is added to it. A black precipitate of lead sulphide indicates the presence of sulphur



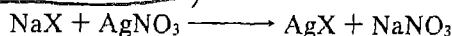
(b) Lassaigne's solution is treated with sodium nitroprusside solution. A violet colour indicates the presence of sulphur. This colour slowly fades on standing



If sulphur is present along with nitrogen and sodium thiocyanate is formed during fusion due to insufficient sodium, then a blood red colouration appears on heating with ferrous sulphate, which is invariably contaminated with ferric sulphate.



*Test for Halogens* Lassaigne's solution is boiled with dilute nitric acid to decompose sodium cyanide or sodium sulphide (if present) to hydrogen cyanide and hydrogen sulphide gases, respectively. This solution is cooled and silver nitrate solution added. A white precipitate soluble in ammonia shows chlorine, a yellowish precipitate, sparingly soluble in ammonia indicates bromine and a yellow precipitate insoluble in ammonia shows the presence of iodine.



*Test for Phosphorus* Phosphorus is detected by fusing the organic compound with sodium peroxide followed by extraction with water. This aqueous solution is boiled with concentrated nitric acid followed by the addition of ammonium molybdate solution. A yellow solution or precipitate indicates the presence of phosphorus. The yellow precipitate is of ammonium phosphomolybdate  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$

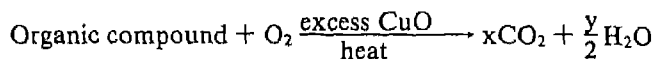
### 18.3 QUANTITATIVE ANALYSIS

Once we have qualitatively determined the presence of various elements in an organic compound, we shall have to quantitatively determine the proportions (or percentages) of these elements in the compound. We shall now discuss the principles

involved in quantitative determinations (estimations) of elements in organic compounds.

### 18.3.1 Carbon and Hydrogen Estimation

A known mass of the organic compound is heated in a current of dry oxygen (free from carbon dioxide) in the presence of cupric oxide till all the carbon is oxidised to carbon dioxide and all the hydrogen is oxidised to water.



Water and carbon dioxide thus produced are absorbed in U-tubes. The one containing anhydrous calcium chloride or anhydrous magnesium perchlorate is for absorbing water and the other, having a strong solution of potassium hydroxide or ascarite (NaOH-CaO) is for absorbing carbon dioxide. The containers (with the absorbents) are weighed before the combustion is performed. The increase in the mass after the experiment would give the amount of water and carbon dioxide produced (Fig. 18.6).

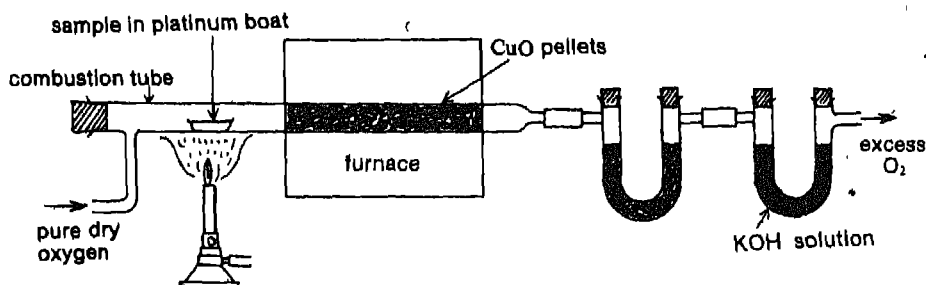


Fig. 18.6 Apparatus for estimation of carbon and hydrogen

Let the mass of the organic compound taken be  $W$  g, increase in the calcium chloride U-tube (i.e., mass of water formed) be  $W_1$ g, and increase in mass of potash U-tube be  $W_2$ g, (i.e., mass of CO<sub>2</sub> formed).

44 g of CO<sub>2</sub>  $\equiv$  12 g of carbon

$$\text{Percentage of carbon} = \frac{12}{44} \times \frac{W_2}{W} \times 100$$

18 g of H<sub>2</sub>O  $\equiv$  2g of hydrogen

$$\text{Percentage of hydrogen} = \frac{2}{18} \times \frac{W_1}{W} \times 100$$

### 18.3.2 Nitrogen Estimation

Nitrogen can be estimated by either of the two methods. (i) Dumas' method, (ii) Kjeldahl's method

(i) *Dumas' Method*: A known mass of the organic compound is heated with cupric oxide in an atmosphere of carbon dioxide. The carbon and hydrogen are oxidised to carbon dioxide and water respectively while nitrogen is set free. If any oxide of nitrogen is produced during this process, it is reduced back to free nitrogen by passing over a heated copper gauze. This gaseous mixture is collected over an aqueous solution of potassium-hydroxide. All the gases except nitrogen are absorbed in the solution (Fig. 18.7) The volume of gas collected is measured and this is equivalent to the nitrogen set free from the compound

Let the mass of the organic compound be  $W$  g

$$\begin{aligned}\text{Volume of nitrogen collected} &= V_1 \text{ cm}^3 \\ \text{Atmospheric pressure} &= P_1 \text{ mm Hg} \\ \text{Room temperature} &= T_1 \text{ K}\end{aligned}$$

$$\begin{aligned}\text{Volume of nitrogen at STP} &= \frac{P_1 V_1 \times 273}{760 \times T_1} \\ &= A \text{ cm}^3\end{aligned}$$

$$\text{Mass of } A \text{ cm}^3 \text{ of nitrogen at STP} = \frac{28 \times A}{22400} \text{ g}$$

$$\text{Percentage of nitrogen} = \frac{28 A \times 100}{22400 \times W}$$

(ii) *Kjeldahl's Method*. Many nitrogen containing organic compounds when heated

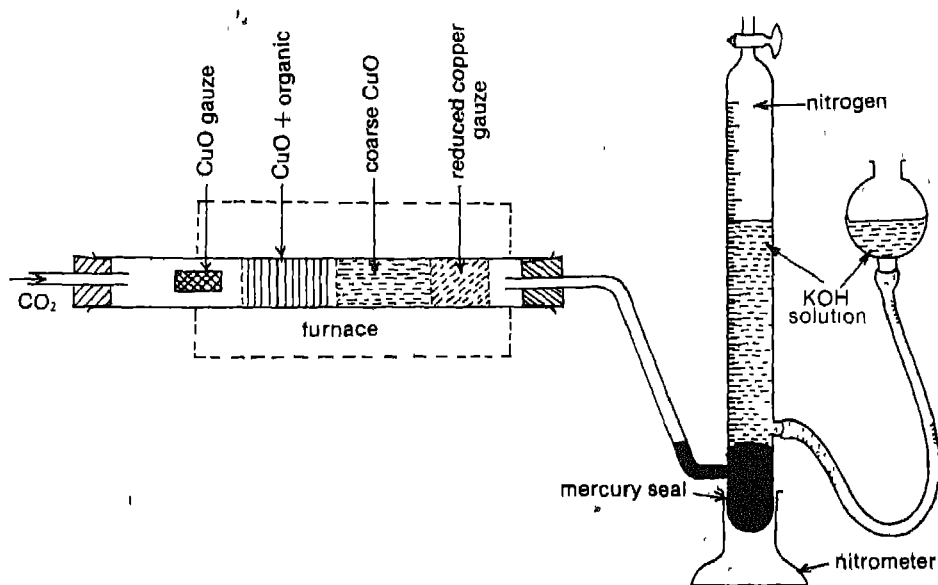


Fig. 18.7 Apparatus for the estimation of nitrogen by Dumas method

strongly with concentrated sulphuric acid are converted quantitatively into ammonium sulphate (Fig. 18.8a).

The solution is heated with excess of sodium hydroxide (Fig. 18.8b). The ammonia gas thus liberated is absorbed in a known volume (taken excess) of a standard solution of acid. The amount of acid neutralised can be determined by titrating the solution against a standard alkali solution and this would correspond to the amount of ammonia produced.

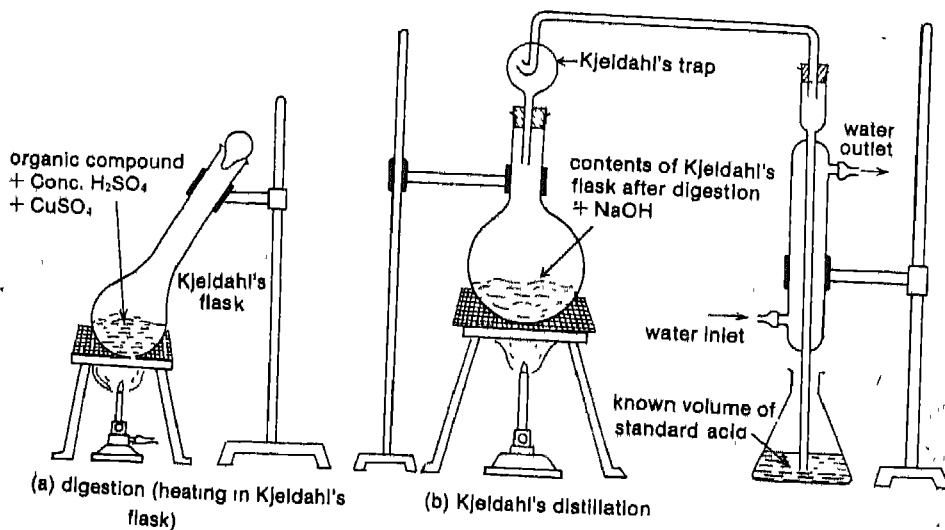
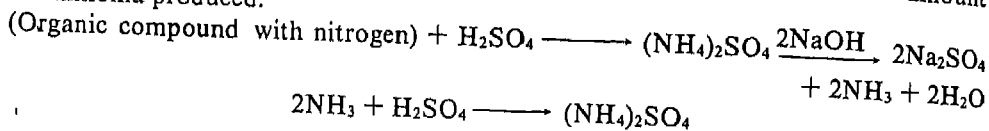


Fig. 18.8 Apparatus for the estimation of nitrogen by Kjeldahl's method

Let the mass of the organic compound taken be  $W$  g

Amount of acid of normality  $N_1$

neutralised by ammonia

But  $1000 \text{ cm}^3$  of normal ammonia

$V_1 \text{ cm}^3$  of  $N_1$  acid

$\equiv \frac{14}{1000} \times V_1 \times N_1$  g of nitrogen

$\therefore$  Percentage of nitrogen

$$\begin{aligned} &= V_1 \text{ cm}^3 \\ &\equiv 17 \text{ g of ammonia} \\ &\equiv 14 \text{ g of nitrogen} \\ &\equiv V_1 \text{ cm}^3 \text{ of } N_1 \text{ ammonia} \\ &\equiv \frac{14V_1N_1}{1000} \text{ g of nitrogen} \\ &= \frac{14V_1N_1}{1000} \times \frac{100}{W} \end{aligned}$$

### 18.3.3 Halogen Estimation

A known mass of an organic compound is heated with fuming nitric acid in the presence of silver nitrate in a special tube known as Carius tube (Fig. 18.9). Carbon and hydrogen are oxidised to carbon dioxide and water while halogen forms a precipitate of silver halide ( $\text{AgX}$ ). After filtration and washing, the precipitate is dried and weighed.

Let the mass of the compound be  $W$  g

Let the mass of the  $\text{AgX}$  formed be  $W_1$  g

Molecular mass of  $\text{AgX} \equiv$  atomic mass of  $X$

$$\therefore \text{Mass of halogen in } W_1 \text{ g of } \text{AgX} = \frac{\text{atomic mass of } X \times W_1}{\text{molecular mass of } \text{AgX}} \text{ g}$$

$$\therefore \text{Percentage of halogen} = \frac{\text{atomic mass of } X \times W_1}{\text{molecular mass of } \text{AgX}} \times \frac{100}{W}$$

### 18.3.4 Other Elements

(a) *Sulphur Estimation:* Sulphur present in an organic compound is oxidised in a Carius tube (Fig 18.9) by fuming nitric acid into sulphuric acid which is then quantitatively precipitated as barium sulphate by the addition of excess barium chloride. The precipitate is filtered, washed, dried and weighed.

Let the mass of the organic compound be  $W$  g

Let the mass of the precipitate be  $W_1$  g

$\cdot$  233 g of  $\text{BaSO}_4 \equiv 32$  g of sulphur

$$\therefore W_1 \text{ g of } \text{BaSO}_4 \equiv \frac{32}{233} \cdot W_1 \text{ g}$$

$$\text{Percentage of sulphur} = \frac{32}{233} \cdot \frac{W_1}{W} \cdot 100$$

(b) *Phosphorus Estimation:* A known mass of the organic substance is heated with fuming nitric acid. The phosphorus present is oxidised to phosphoric acid. The phosphoric acid thus obtained is treated with magnesia mixture\* to give a precipitate  $\text{MgNH}_4\text{PO}_4$  which on ignition is converted into  $\text{Mg}_2\text{P}_2\text{O}_7$ .

\* Magnesia mixture is a solution containing magnesium chloride, ammonium chloride and a little ammonia

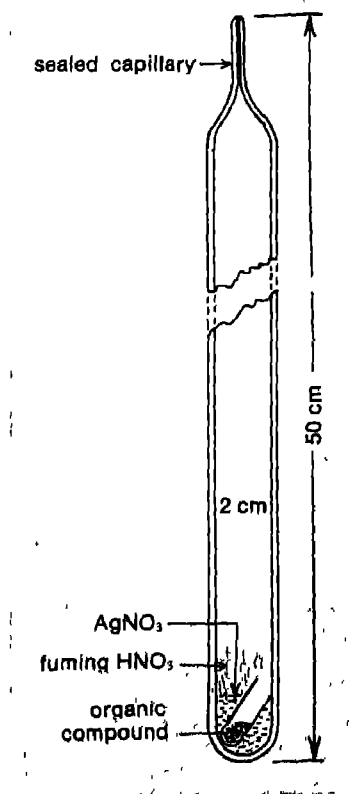


Fig 18.9 A Carius tube for estimation of halogens

Let the mass of the organic compound be  $W$  g  
 Mass of  $Mg_2P_2O_7$  obtained on ignition =  $W_1$  g  
 $222$  g of  $Mg_2P_2O_7 \equiv 62$  g of P

$$\text{Percentage of phosphorus} = \frac{62}{222} \times \frac{W_1}{W} \times 100$$

(c) *Estimation of Oxygen*: The percentage of oxygen in an organic compound is normally obtained by subtracting the sum of the percentages of all other elements from 100.

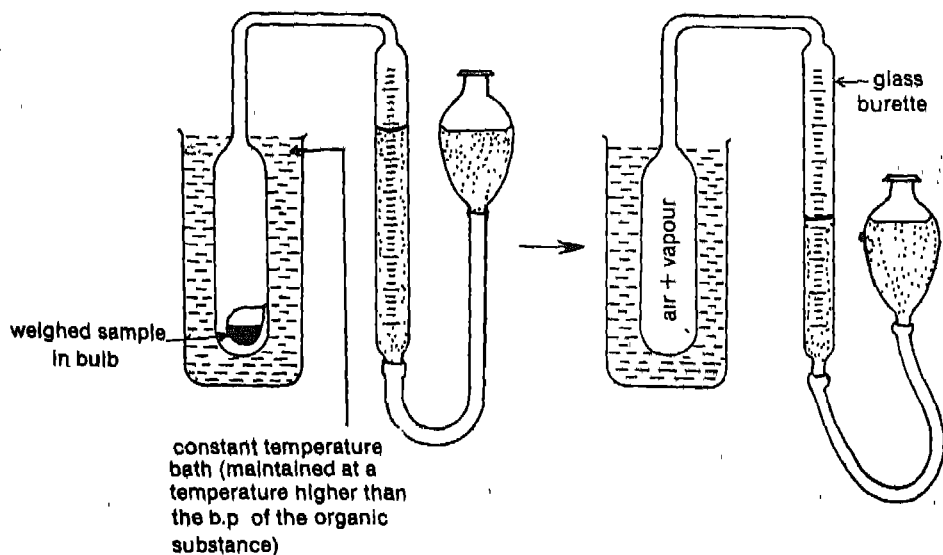
A few decades ago, large amounts (about 1 g or more) of the pure compounds were needed for quantitative analysis. Now-a-days, the techniques have become so refined and precise that a complete analysis can be done with only 3 to 4 mg of the substance. These analyses are generally accurate within  $\pm 0.03\%$ . Automatic analysers for carbon, hydrogen and nitrogen give very quick analysis (in a few minutes).

#### 18.4 DETERMINATION OF MOLECULAR MASS

Molecular mass of organic compounds are determined by a number of methods. This information becomes essential to fix the molecular formulae of compounds. We shall now discuss the principles of some of these methods.

##### 18.4.1 Victor Meyer's Method

This is a convenient method for the determination of molecular masses of volatile substances. A known mass of a substance is converted into vapour. The vapour is



**Fig. 18.10** Diagrammatic representation of Victor Meyer's apparatus for determination of vapour density of a volatile substance



made to displace an equal volume of air which can be collected over water. The apparatus employed in Victor Meyer's procedure is diagrammatically shown in Fig. 18.10.

Let the mass of the organic compound be  $W$  g

Volume of air displaced =  $V_1$  cm<sup>3</sup>

Pressure of the air =  $P$  mm Hg

Room temperature =  $T_1$  K

Volume,  $V_2$  of air displaced at STP,

$$= \frac{P \times V_1 \times 273}{T_1 \times 760} = \text{volume of vapour at STP}$$

Thus,  $V_2$  cm<sup>3</sup> of the vapour of the substance at STP weighs =  $W$  g

Therefore, 22,400 cm<sup>3</sup> of vapour of the substance at STP should

$$\text{weigh} = \frac{W \times 22,400}{V_2}$$

$$\text{Molecular mass of the substances} = \frac{W \times 22,400}{V_2}$$

#### 18.4.2 Molecular Mass by Elevation of Boiling Point or Depression of Freezing Point

If an organic compound is non-volatile, its molecular mass can be determined by measuring depression in freezing point or the elevation in boiling point of a solvent caused by dissolving a known mass of the substance (solute) in a known mass of the solvent. The principles of these methods will be discussed in class XII

#### 18.4.3 Volumetric Method

This is applicable to acids as well as to bases. A known mass of the acid is dissolved in water or neutral alcohol and titrated against standard alkali solution using phenolphthalein as indicator.

Let  $V_1$  cm<sup>3</sup> of  $N_1$  alkali be used for neutralisation of  $W$  g of the acid

Then  $V_1$  cm<sup>3</sup> of  $N_1$  alkali  $\equiv$   $W$  g of acid

$$1000 \text{ cm}^3 \text{ of } N \text{ alkali} = \frac{W}{V_1} \times \frac{1000}{N_1}$$

$$\text{Molecular mass} = \frac{W}{V_1} \times \frac{1000}{N_1} \times \text{basicity of acid}$$

### 18.5 CALCULATION OF EMPIRICAL AND MOLECULAR FORMULAE

The empirical formula of a compound is defined as the simplest formula that shows the ratio of the atoms of various elements in a molecule. This is normally calculated from the percentage composition of the elements in the molecule according to the following rules:

1. The percentages of all the elements are divided by their respective atomic masses.

2. The numbers thus obtained are divided by the lowest of the above numbers. The quotients are normally whole numbers. If they are not whole numbers, they are converted to whole numbers by multiplication with a suitable common factor.

Let us take an example where we need to calculate the empirical formula of an organic compound which has 61.00% of carbon and 11.88% of hydrogen. Now the sum of the percentage of carbon and hydrogen is less than 100. So the third element must be oxygen having percentage =  $100 - (61.00 + 11.88) = 27.12\%$ .

The empirical formula is then calculated as follows.

Element	Percentage	Relative No. of atoms	Dividing by smallest factor	Simple whole No. ratio
Carbon	61.00	$\frac{61.00}{12} = 5.08$	$\frac{5.08}{1.70} = 2.99$	3
Hydrogen	11.88	$\frac{11.88}{1} = 11.88$	$\frac{11.88}{1.70} = 6.9$	7
Oxygen	27.12	$\frac{27.12}{16} = 1.70$	$\frac{1.70}{1.70} = 1$	1

Empirical formula  $C_3H_7O$

The molecular formula of a compound gives the actual number of atoms of each element present in the molecule. The molecular formula may be the same as the empirical formula or a simple multiple of it.

$$\text{Molecular formula} = \text{Empirical formula} \times n$$

$$\therefore n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$$

In the problem on empirical formula worked out earlier, if the molecular mass of the compound is 118, the value of  $n$  will be 2. This is because the empirical formula ( $C_3H_7O$ ) mass is 59 and  $n = 118/59 = 2$ . The molecular formula is therefore  $C_6H_{14}O_2$ .

## 18.6 SOME WORKED OUT EXAMPLES IN ORGANIC QUANTITATIVE ANALYSIS

### Example 18.1

In a Dumas nitrogen estimation method, 0.30 g of an organic compound gave  $50 \text{ cm}^3$  of nitrogen collected at 300 K and 715 mm pressure. Calculate the percentage composition of nitrogen in the compound (vapour pressure of water at 300 K is 15 mm).

*Solution:*

Volume of nitrogen	= 50 cm <sup>3</sup>
Temperature	= 300 K
Pressure	= 715 mm
Vapour pressure of water	= 15 mm
Actual pressure over the gas	= (715 — 15) = 700 mm

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \text{or} \quad \frac{700 \text{ mm} \times 50 \text{ cm}^3}{300 \text{ K}} = \frac{760 \text{ mm} \times V_2}{273 \text{ K}}$$

$$V_2 = \frac{273 \times 700 \times 50}{300 \times 760} = 41.9 \text{ cm}^3$$

22,400 cm<sup>3</sup> of nitrogen at STP weighs 28 g

$$41.9 \text{ cm}^3 \text{ of nitrogen at STP will weigh} = \frac{28 \times 41.9}{22,400} \text{ g}$$

$$\text{Therefore percentage of nitrogen} = \frac{28 \times 41.9 \times 100}{22,400 \times 0.3} = 17.46\%$$

*Example 18.2*

0.50 g of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 cm<sup>3</sup> of 1N H<sub>2</sub>SO<sub>4</sub>. The residual acid required 60 cm<sup>3</sup> of N/2 NaOH solution. Find the percentage of nitrogen in the compound.

*Solution:*

$$60 \text{ cm}^3 \text{ of N/2 NaOH} = 60 \text{ cm}^3 \text{ of N/2 H}_2\text{SO}_4 \\ = 30 \text{ cm}^3 \text{ of N H}_2\text{SO}_4$$

$$\text{Amount of normal H}_2\text{SO}_4 \text{ consumed by ammonia} \\ = (50 - 30) \text{ cm}^3 = 20 \text{ cm}^3$$

$$20 \text{ cm}^3 \text{ of N H}_2\text{SO}_4 = 20 \text{ cm}^3 \text{ of N NH}_3 \text{ solution}$$

$$1000 \text{ cm}^3 \text{ of N NH}_3 \text{ solution contains 14 g of nitrogen}$$

Therefore 20 cm<sup>3</sup> of N NH<sub>3</sub> solution will contain

$$= \frac{14 \times 20}{1000} = 0.28 \text{ g of nitrogen}$$

Thus, 0.5 g of the organic compound contains 0.28 g of nitrogen. Therefore percentage of nitrogen is

$$= \frac{0.28 \times 100}{0.50} = 56\%$$

*Example 18.3*

0.15 g of an organic compound gave 0.12 g of AgBr by the Carius method. Find the percentage of bromine in the compound.

*Solution:*

$$\text{Molecular mass of AgBr} = 108 + 80 = 188 \text{ g/mol}$$

$$188 \text{ g of AgBr contains 80 g of bromine}$$

Therefore 0.12 g of AgBr will contain  $\frac{80 \times 0.12}{188}$

$$= 0.051 \text{ g of bromine}$$

Therefore, percentage of bromine in the compound

$$= \frac{0.051 \times 100}{0.15} = 34\%$$

#### Example 18.4

4. 0.35 g of a volatile liquid in the Victor Meyer's method displaced 86.5 cm<sup>3</sup> of air at S.T.P. Calculate the molecular mass of the liquid.

*Solution :*

Volume of the liquid vapour = volume of the air displaced  
= 86.5 cm<sup>3</sup> at S.T.P.

86.5 cm<sup>3</sup> of the vapour weighs 0.35 g

Therefore 22,400 cm<sup>3</sup> of the vapour weighs  $= \frac{0.35 \times 22,400}{86.5} = 90.64 \text{ g}$

But 22,400 cm<sup>3</sup> is the volume occupied by the molecular mass of the liquid at S.T.P.

Therefore the molecular mass of the liquid = 90.64

#### Example 18.5

5. On analysis, 0.2 g of a monobasic acid gave 0.505 g of CO<sub>2</sub> and 0.0864 g of H<sub>2</sub>O. 0.305 g of this acid required 25 cm<sup>3</sup> of N/10 sodium hydroxide for neutralisation. Find the molecular formula of the acid.

*Solution :*

To solve this problem, the empirical formula is first calculated. The molecular mass is obtained using the volumetric data. Together, these two can be employed to determine the molecular formula of the acid.

a) Calculation of empirical formula

Weight of the sample used for analysis = 0.20 g

Weight of carbon dioxide obtained = 0.505 g

44 g of carbon dioxide contains 12 g of carbon

Therefore 0.505 g of carbon dioxide contains

$$= \frac{0.505 \times 12}{44}$$

$$= 0.138 \text{ g of carbon}$$

Therefore percentage of carbon  $= \frac{0.138 \times 100}{0.2}$

$$= 69\%$$

Weight of water obtained = 0.0864 g

18 g of water contains 2g of hydrogen

$$\text{Therefore 0.0864 g of water contains} = \frac{0.0864 \times 2}{18}$$

$$= 0.0096 \text{ g of hydrogen}$$

$$\text{Therefore percentage of hydrogen} = \frac{0.0096 \times 100}{0.2}$$

$$= 4.8\%$$

As the percentages of carbon and hydrogen add up to 73.8%, oxygen should constitute the remainder. Therefore the percentage of oxygen =  $100 - 73.8 = 26.2\%$ .

As explained in Section 18.5 the empirical formula is calculated

Element	Percentage	Relative No of atoms	Dividing by smallest factor	Simple whole No ratio
Carbon	69.00	$\frac{69.00}{12} = 5.75$	$\frac{5.75}{1.64} = 3.51$	7
Hydrogen	4.80	$\frac{4.80}{1} = 4.80$	$\frac{4.80}{1.64} = 2.93$	6
Oxygen	26.20	$\frac{26.20}{16} = 1.64$	$\frac{1.64}{1.64} = 1.00$	2

Therefore the empirical formula is  $C_7H_6O_2$

b) Calculation of the molecular mass

0.305 g of acid requires 25 cm<sup>3</sup> of N/10 sodium hydroxide for neutralisation.

25 cm<sup>3</sup> of N/10 sodium hydroxide = 0.305 g of acid

$$\text{Therefore 1000 cm}^3 \text{ of N sodium hydroxide} = \frac{0.305 \times 1000}{25 \times 0.1}$$

$$= 122 \text{ g of acid}$$

Therefore the molecular mass of the acid =  $122 \times \text{basicity}$

$$= 122 \times 1 = 122$$

Therefore the molecular formula = Empirical formula  $\times n$

$$\text{where } n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$$

$$\text{Empirical formula mass} = 7 \times 12 + 6 \times 1 + 2 \times 16 = 122$$

$$\text{Therefore } n = \frac{122}{122} = 1$$

Therefore the molecular formula of the acid is  $C_7H_6O_2$

## 18.7 MODERN METHODS OF STRUCTURE ELUCIDATION

The rapid development of scientific instrumentation has progressed to a point that the complete structure of a compound can be obtained in a matter of days. Molecular weights and molecular formulae are readily determined from mass spectro-

metry. The types of functional groups present in a molecule are found from electronic, infra-red and nuclear magnetic resonance spectroscopies. Finally, the complete three dimensional structure of the molecule, including bond lengths and bond angles is determined from X-ray diffraction. In contrast to the classical methods discussed in this Unit, these methods need very small amounts of the sample. All these methods have made the structure determination of a compound a much simpler task than it was a few decades ago. A detailed discussion of the scope and application of these methods is beyond the scope of this book.

### EXERCISES

- 18.1 Explain with an example the following terms:  
 (i) crystallisation, (ii) sublimation, (iii) simple distillation, (iv) fractional distillation, (v) distillation under reduced pressure, (vi) steam distillation, (vii) extraction with a solvent, (viii) chromatography.
- 18.2 (i) Will you get any precipitate if you add silver nitrate solution to chloromethane? If not, why?  
 (ii) Write the chemical equations involved in the detection of nitrogen, halogens, sulphur and phosphorus, present in an organic compound.
- 18.3 0.45 g of an organic compound gave on combustion 0.792 g of  $\text{CO}_2$  and 0.324 g of water. 0.24 g of the same substance was kjeldahlised and the ammonia formed was absorbed in 50.0  $\text{cm}^3$  of  $\text{N}/4 \text{ H}_2\text{SO}_4$ . The excess acid required 77.0  $\text{cm}^3$  of  $\text{N}/10 \text{ NaOH}$  for complete neutralisation. Calculate the empirical formula of the compound.
- 18.4 0.45 g of an organic compound containing only carbon, hydrogen and nitrogen on combustion, gave 1.1 g of carbon dioxide and 0.3 g of water. What is the empirical formula of the compound?
- 18.5 What is the empirical formulae of the compounds whose analysis percentages are given below  
 (i) C = 41.35, H = 6.89, N = 24.12  
 (ii) C = 60, H = 13.3  
 (iii) C = 65.73, H = 15.06, N = 19.21  
 (iv) C = 50.4, H = 9.25  
 (v) C = 10, H = 0.84, Cl = 89.2  
 (vi) C = 71.4, H = 3.78, N = 7.57, S = 17.3  
 (vii) C = 28.2, H = 1.57, S = 12.5, Cl = 13.9, Br = 31.2  
 (viii) C = 39.2, H = 9.79, P = 33.7
- 18.6 1.01 g of an organic compound containing 41.37% carbon and 5.75% of hydrogen on kjeldahlising, required 11.6  $\text{cm}^3$  of  $\text{N}/10 \text{ HCl}$ . In Carius determination 0.2006 g of the substance gave 0.5544 g of barium sulphate. Find the formula of the compound.
- 18.7 A compound (molecular mass 147) contains 49.0% carbon and 2.72% hydrogen. 2.561 mg of the compound gave 5.00 mg of silver chloride in Carius estimation. Find the molecular formula of the compound.

- 18.8 0.246 g of an organic compound containing 58.53% carbon and 4.06% hydrogen gave 22.4 cm<sup>3</sup> of nitrogen at STP. What is the empirical formula of the compound?
- 18.9 0.246 g of an organic compound gave 0.198 g of carbon dioxide and 0.1014 g of water on complete combustion. 0.37 g of the compound gave 0.638 g of silver bromide. What is the molecular formula of the compound if its vapour density is 54.4?
- 18.10 0.1 g of an organic monobasic acid gave 0.2545 g of CO<sub>2</sub> and 0.04428 g H<sub>2</sub>O on combustion. 0.122 g of the acid required for neutralisation 10 cm<sup>3</sup> of a N/10 alkali. Determine the molecular formula of the acid.
- 18.11 An acid of mol. mass 104 contains 34.6% carbon, and 3.85% hydrogen. 3.812 mg of the acid required 7.33 cm<sup>3</sup> of 0.01 N NaOH for neutralisation. Suggest a structure for the acid.
-

## UNIT 19

# THE MOLECULES OF LIFE

*Living forms are composed of cells  
and cells are factories of chemicals*

### OBJECTIVES

After studying this Unit, we shall be able to:

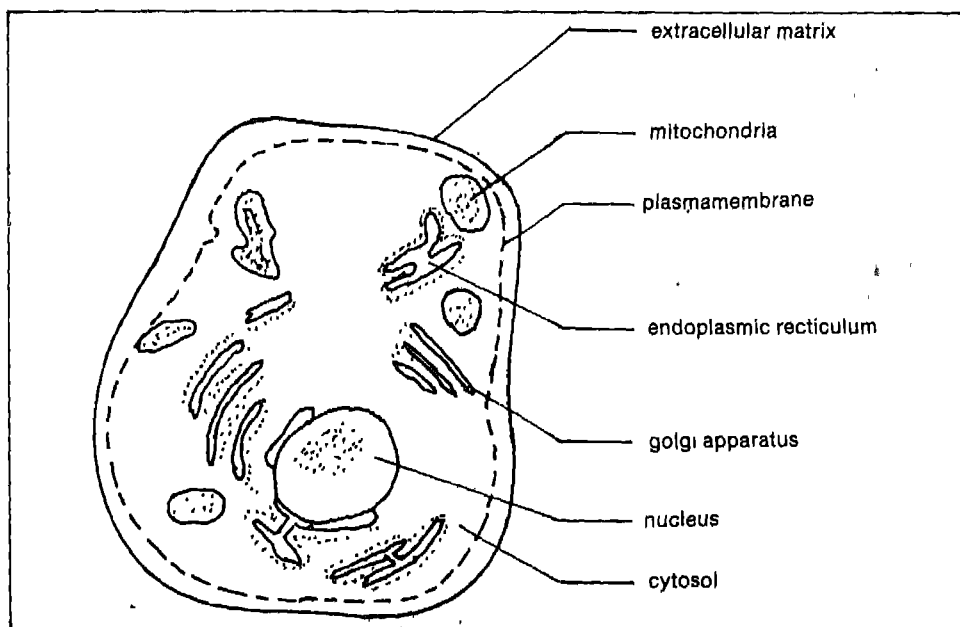
- \* list the basic chemical constituents of a cell;
- \* know the natural sources of carbohydrates and their chemical composition,
- \* name the important functions of proteins;
- \* define the primary, secondary and tertiary structure of proteins;
- \* understand the basic properties of fibrous proteins such as silk, wool, hair from chemical structure;
- \* explain the importance of enzymes;
- \* know the basic composition of nucleic acids;
- \* explain the double helical structure of DNA;
- \* describe the two important biological functions of nucleic acids;
- \* explain how viruses cause disease;
- \* describe the chemical constituents of cell membranes.



IN THE PREVIOUS UNITS, we studied the various types of simple organic molecules and their chemical reactions. In this Unit, we shall study molecules which form the basis of life and which are more complex in structure

### 19.1 THE CELL

All living creatures are made of cells. Cells are the smallest units of life. They are indeed very small and are invisible to the naked eye. They were first seen over 300 years ago, soon after the construction of the first microscope. Cells (Figure 19.1) are essentially packets of chemicals necessary for life, enclosed in an envelope known as cell membrane. The most important characteristic of a cell is its ability to grow and divide to provide daughter cells. These likewise are capable of generating new progeny cells



**Fig. 19.1** Structural component of a cell. The outer boundary of the cell plasma membrane separates the extracellular matrix and the cytoplasm of the cell. Golgi apparatus is a membrane bound, flat sac which is packed with macromolecules for secretion and delivery to other organelles. The endoplasmic reticulum present in eukaryotic cells contains on its outer surface ribosomes engaged in protein synthesis. The nucleus contains the chromosomal DNA packed with histone proteins. Mitochondria are the power plants of all eukaryotic cells which harness energy from food to make ATP. Lysosomes contain hydrolytic enzymes involved in intracellular digestion.

A living cell is composed of a restricted set of elements, six of which, C, H, N, O, P and S make up more than 99% of its weight. The most abundant substance in a living cell is water (Table 19.1) which amounts to about 70% of the weight of cells. Next to water, all but a tiny fraction of the cell are carbon compounds. These fall

into two different classes. The first class are the 'small molecules' having molecular masses in the range of 100 to 1000, containing upto 30 carbon atoms. These are found free in solution in the cytoplasm of the cell. They form a pool of intermediates from which the second class of molecules, the 'macro-molecules' are synthesised

TABLE 19 I

## Approximate Chemical Composition of a Bacterial Cell\*

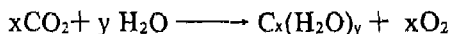
	<i>Percent of total cell weight</i>
Water	70
Inorganic ions ( $\text{Na}^+$ , $\text{K}^+$ , $\text{Mg}^{2+}$ , $\text{Ca}^{2+}$ , $\text{Cl}^-$ , etc)	1
Polysaccharides	2
Proteins	15
Nucleic acids DNA	1
RNA	6
Phospholipids	2
Miscellaneous small molecules	3

\* Total cell volume =  $2 \times 10^{-2} \text{ cm}^3$

The macromolecules in a cell are polymers of very high molecular masses. Among these, the most important are carbohydrates, proteins and nucleic acids. Proteins and carbohydrates constitute two of the three principal classes of our food intake. Carbohydrates serve as energy sources and structural material of plants. Proteins are found in all parts of the body and they have an enormous variety of functions. Some proteins are structural components of skin, muscle and hair. Others control the transmission of nerve impulses; still others are enzymes or biocatalysts which accelerate many reactions in cells. The deoxy ribo nucleic acid, DNA, is the molecule in which an organism stores information about its genetic characteristics for transmission from generation to generation.

## 19.2 CARBOHYDRATES

Carbohydrates occur widely in nature. Among its many forms are starch, cotton, table sugar and wood. Besides carbon, they consist of hydrogen and oxygen in a ratio 2:1, as in water itself. Thus these are the 'hydrates of carbon' represented by the general formula  $\text{C}_x(\text{H}_2\text{O})_y$  where  $x$  and  $y$  are integers. They are synthesised by green plants from  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the presence of sunlight by a process called PHOTOSYNTHESIS.



Carbohydrates can be classified into three main groups: MONOSACCHARIDES, DISACCHARIDES and POLYSACCHARIDES. Monosaccharides or simple sugars, are carbohydrates that cannot be broken into smaller units upon hydrolysis. They comprise mainly of C3 to C7-carbon compounds. Disaccharides produce two monosaccharide units on hydrolysis. Polysaccharides produce a number of sugar units on hydrolysis.

## 19.2.1 Monosaccharides

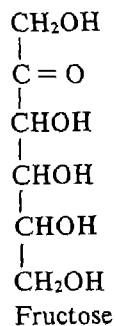
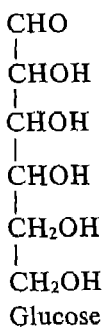
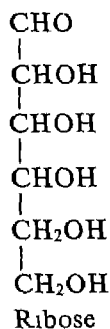
There are about twenty monosaccharides which occur naturally. All monosaccharides are polyhydroxy compounds as they possess a number of alcoholic groups. In addition, they also contain either an aldehyde ( $\text{H}-\text{C}=\text{O}$ ) or a keto ( $>\text{C}=\text{O}$ ) function. Depending upon the number of carbon atoms they possess (Table 19.2), the monosaccharides may be subdivided as TRIOSSES, TETROSES, PENTOSES, HEXOSES or HEPTOSES. They are also designated as ALDOSES or KETOSSES depending on whether they contain aldehyde or ketone groups.

TABLE 19.2  
Monosaccharides

<i>Class</i>	<i>Molecular Formula</i>	<i>Examples</i>
Trioses	$\text{C}_3\text{H}_6\text{O}_3$	Glycerose
Tetroses	$\text{C}_4\text{H}_8\text{O}_4$	Erythrose
Pentoses	$\text{C}_5\text{H}_{10}\text{O}_5$	Ribose
Hexoses	$\text{C}_6\text{H}_{12}\text{O}_6$	Glucose, Fructose

The monosaccharides are highly soluble in water due to the presence of a number of hydroxyl groups. They are sweet in taste and char on heating. They show chemical reactions characteristic of both hydroxyl and carbonyl groups.

The trioses are formed during the course of metabolic breakdown of the hexoses. The most important monosaccharides are ribose, glucose and fructose. The  $\text{C}_5$  sugar RIBOSE, is an important chemical constituent of the nucleic acids.



**Glucose.** This aldose sugar occurs abundantly in plants and animals. It is found in juices of fruits, saps and plants, blood and tissue of animals. It is the immediate source of energy for energy requiring cellular reactions in the body such as tissue repair, macromolecular synthesis, muscle movements, etc. An average adult has five to six grams of glucose in his blood. This is sufficient to supply energy for about fifteen minutes and is continuously replaced in the body. Urine usually contains a trace of glucose, but its concentration is greatly increased in the urine of untreated diabetes patients. Glucose occurs in two isomeric forms:  $\alpha$  and  $\beta$ . It is the major

structural component of some important higher saccharides such as SUCROSE, MALTOSE and LACTOSE.

**Fructose:** This is a ketose monosaccharide which is also present in honey and fruit juices. It can be converted into glucose in the liver and intestine and hence used in the body. It is the sweetest of all the monosaccharides.

### 19.2.2 Disaccharides

The disaccharides are sugars which can be hydrolysed into two monosaccharides (Table 19.3). The three most important monosaccharides are maltose, lactose, and sucrose. Maltose or malt sugar is obtained from partial hydrolysis of starch and consists of two glucose units joined together. Sucrose or table sugar is isolated from the juice or sap of plants such as sugarcane, sugar beet, pineapple and carrot roots.

TABLE 19.3

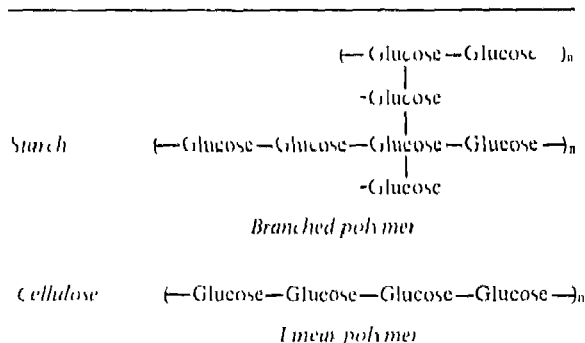
#### Disaccharides

<i>Disaccharides</i>	<i>Monosaccharide components</i>
Maltose	Glucose + Glucose
Sucrose	Glucose + Fructose
Lactose	Glucose + Galactose

The hydrolysis of sucrose by acid or enzyme gives its monosaccharide components which are an equimolar mixture of glucose and fructose. The mixture is called 'invert sugar' and honey is a rich natural source of invert sugar. The gooey syrup that bathes chocolates is also invert sugar. Lactose or milk sugar occurs to about 5% in cow's milk and 7% in human milk.

### 19.2.3 Polysaccharides

Polysaccharides are polymers in which the monomeric units are the monosaccharides. The two important polysaccharides are STARCH and CELLULOSE (Table 19.4).

TABLE 19.4  
Polysaccharides

Starch is a polymer consisting entirely of  $\alpha$ -glucose units and is the major storage form of glucose in plants. It is the most important food source of carbohydrate and is found in cereals, potatoes, legumes and other vegetables. Cellulose is the chief structural component of wood and other plants. It accounts for more than one-half of the constituents of all living matter. Cotton is made up of 80% cellulose. The monomeric unit in cellulose is  $\beta$ -glucose as compared to the  $\alpha$ -glucose units of starch. This difference has a tremendous effect on the chemical structure and properties of cellulose and starch. Cellulose is a linear polymer and mechanically much stronger than starch which occurs as a branched polymer.

Humans do not possess the enzymes necessary to break down cellulose into glucose and hence are unable to digest cellulose. Animals such as cow and deer have intestinal bacteria that produce necessary enzymes for breaking down cellulose into glucose. If chemists could find a simple way to break cellulose down to glucose, we would have another important source of food.

### 19.3 PROTEINS

Proteins are the most complex of all macromolecules found in living cells. They are very vital to living organisms as they perform a wide variety of biological functions. In addition they are also structural components of certain tissues. Some of the important proteins and their functions are given in Table 19.5.

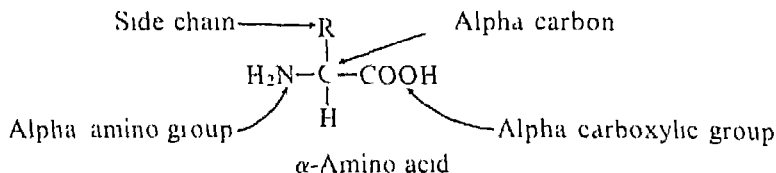
TABLE 19.5

<i>Type</i>	<i>Examples</i>	<i>Function</i>
Enzymes	Trypsin, pepsin	Catalysis of biochemical reactions
Transport	Haemoglobin	Transport of oxygen from lungs to various tissues through blood stream
Storage	Myoglobin	Stores oxygen in muscles until it is needed for energy production
Motion	Myosin, Actin	Involved in muscle movement
Structural	Collagen, Keratin	Structural and protective function occurs in hairs, nails, teeth, etc
Information transmission	Insulin, Glucagon	Hormones

Proteins are polymers and the monomeric units in them are the amino acids.

#### 19.3.1 Amino Acids

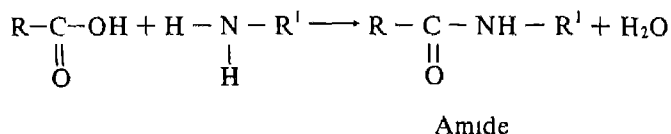
Amino acids are molecules that have both an amino ( $-\text{NH}_2$ ) and a carboxylic ( $-\text{COOH}$ ) group. The amino acids in proteins are called  $\alpha$ -amino acids because they have both the amino and carboxylic groups attached to the same carbon atom.



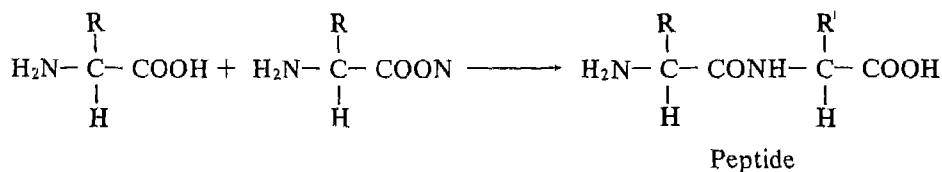
There are about 20 naturally occurring amino acids that are part of protein structures. They all differ in the chemical nature of the side chain R. The simplest amino acid is GLYCINE, for which  $R = H$ ; when  $R = CH_3$ , the amino acid is ALANINE. Some amino acids have aryl side chains and some have hydroxylic, carboxylic, amino or thio groups present in their side chains. The nature of the side chain is important in determining the properties of the resulting proteins

### 19.3.2 Peptide Bond

The product of reaction between a compound containing a carboxylic acid and that with an amino group is called an AMIDE. Amides are



thus compounds containing the chemical functionality  $-CONH-$ . The amide link resulting from reaction between two amino acids is called a PEPTIDE BOND. The



formation of the peptide bond involves only the alpha amino and alpha carboxylic groups and not groups present in the side chain R. More amino acids may be added to a peptide in a similar fashion to obtain long linear polymers of amino acids which are called PROTEINS. Proteins are thus POLYPEPTIDES and may contain 100-400 amino acid units per chain, with molecular masses ranging from 15,000-60,000 or more.

Proteins =  $aa_1 - aa_2 - aa_3 - aa_4 - \dots$

where  $aa$  = amino acid and  $-$  represents a peptide bond

### 19.3.3 Structure of Proteins

The order or sequence in which the various amino acids are linked in protein is called the PRIMARY STRUCTURE of the protein. The differences in chemical and

biological properties of various proteins and peptides arise due to difference in their primary structure. In 1953, the British chemist Frederick Sanger determined the first ever primary structure of a protein, that of INSULIN\* and for this work he was awarded a Nobel Prize. Since then, the primary structures of several hundred proteins have been determined. The importance of the primary structure of a protein is reflected in the fact that, change of just one amino acid in the sequence can disrupt the biological activity of the protein. For example, in *haemoglobin*—the protein in blood which carries oxygen, replacement of one specific amino acid results in defective haemoglobin. This causes a disease called sickle cell anaemia. In these patients, the defective haemoglobin in red blood cells precipitates, causing the cells to sickle and sometimes burst.

The long, flexible peptide chains of proteins are folded into relatively rigid regular conformations called the SECONDARY STRUCTURE. This is largely a consequence of hydrogen bonding which can be formed between the C=O and N-H groups of different peptide bonds. The formation of such hydrogen bonding between amide groups within the same chain, causes the peptide chains to coil up into a spiral structure called the  $\alpha$ -helix (Figure 19.2), similar to a corkscrew. This type of structure is adopted by fibrous structural proteins such as those present in wool and hair. These proteins are elastic, i.e., they can be stretched. During this process, the weak hydrogen bonds causing the  $\alpha$ -helix are broken. This tends to increase the length of the helix, like a spring. On releasing the tension, the hydrogen bonds are reformed, giving back the original helical shape.

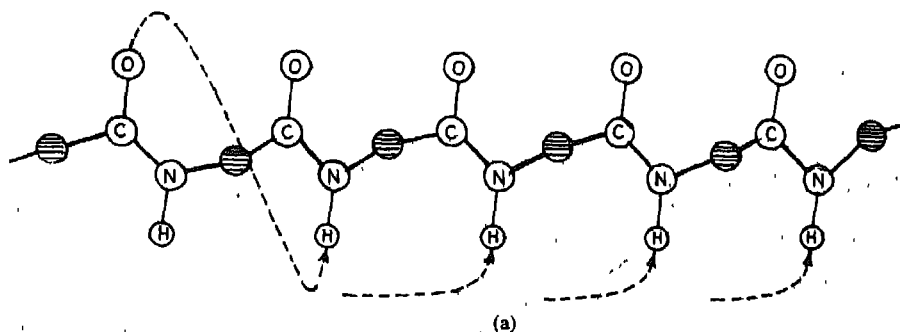
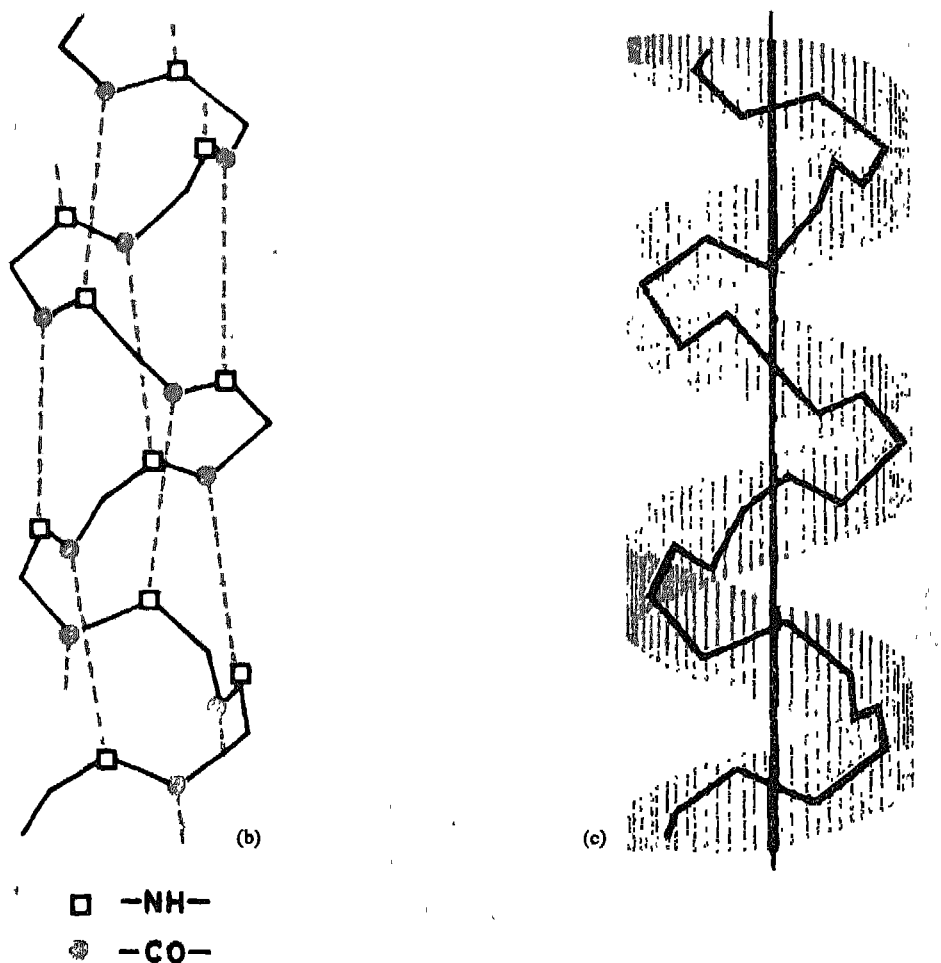


Fig. 19 2(a) (Caption on page 492)

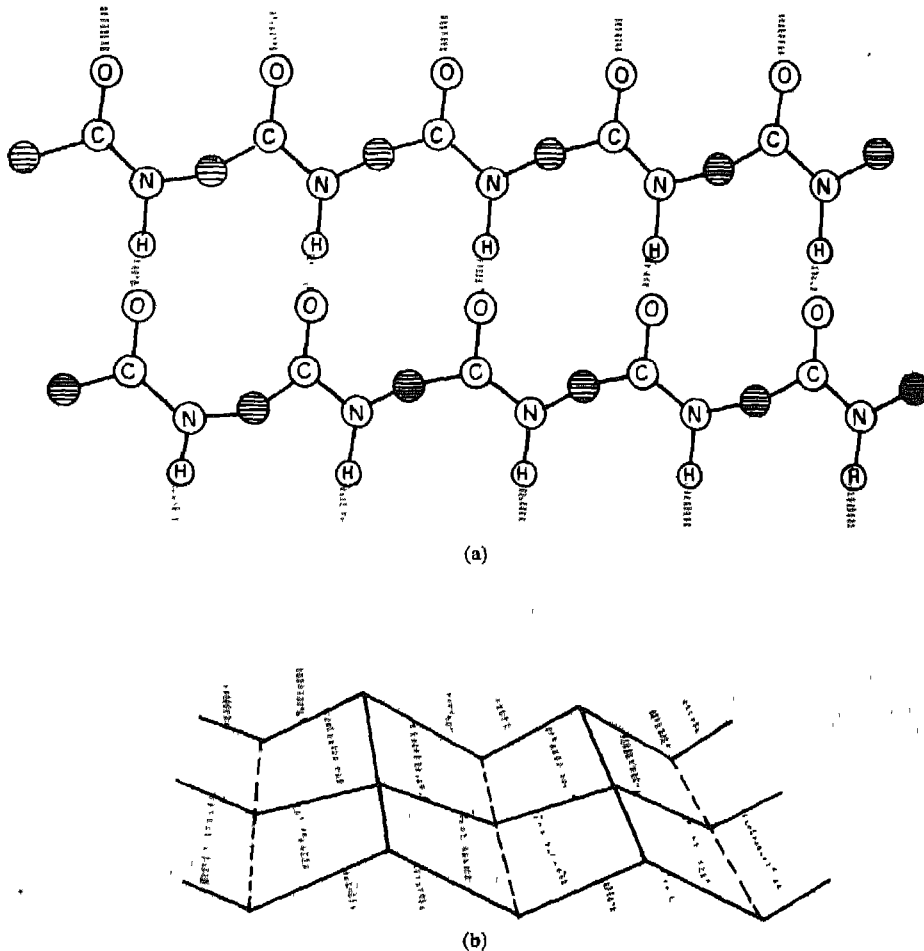
\* Insulin is a peptide hormone produced in the pancreas and is essential to the metabolism of carbohydrates in the body. It contains 51 amino acids arranged in two chains which are cross-linked to each other. Insulin has an important role in maintaining the sugar level in the blood and deficiency of insulin leads to DIABETES. Diabetes is a serious and widespread disease and the diabetic patients have to be administered insulin to regulate their condition.



**Fig 19.2** Structure of helices in proteins (a) Linear peptide chain Dotted lines indicate the possibilities of hydrogen bonding within the same chain between the different peptide groups, Such intrachain hydrogen bonding [ (b) coloured lines ] leads to the folding of peptide chains into helical structures (c) The peptide backbone in a helical structure

A different type of secondary structure is possible, when hydrogen bonds are formed between amide groups of two different protein chains (Figure 19.3) If the proteins are laid parallel to each other, a very large number of  $\text{N-H} \cdots \text{O}=\text{C}$  hydrogen bonds can be formed between the chains. A number of such chains can be interbonded together to form a sheet. These sheets are then stacked one upon another to form a three-dimensional structure called a beta pleated sheet. Silk has a structure of this type which gives it its characteristic mechanical properties. Silk is





**Fig. 19.3** (a) Hydrogen bonding between peptide groups from adjacent chains leads to formation of sheet structures (b) Schematic picture of a  $\beta$ -pleated sheet with hydrogen bonding indicated by coloured lines

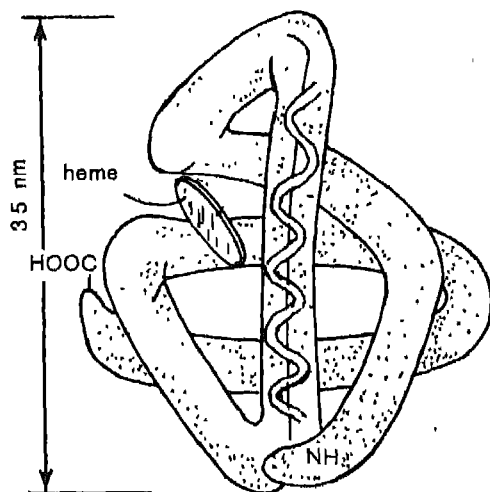
not elastic since stretching leads to pulling the peptide covalent bonds. On the other hand, it can be bent easily, because, during this process, the protein sheets slide over each other. Silk (fibroin), wool (keratin) and hair (collagen) are examples of FIBROUS proteins. They are either long, rod-shaped molecules or sheet-type structures.

#### 19.3 4 Tertiary Structure of Proteins and Denaturation

There are other proteins such as MYOGLOBIN (Figure 19.4) in muscle and HAEMOGLOBIN in blood which have more complex structures. They consist of helices, but the chain is folded up in a complex way to give a compact structure. These proteins

are called GLOBULAR proteins and are more or less spherical in shape. The folding up of chains into a compact form is called the TERTIARY structure of proteins.

The disruption of the tertiary structure (DENATURATION) leads to loss of biological activity and the proteins become insoluble. Proteins are denatured by a variety of reagents including heat, acid, high salt concentrations or heavy metals. Denaturation does not change the primary structure, but results from a rearrangement of secondary and tertiary structures.



**Fig. 19.4** Myoglobin, a protein used to store oxygen in the muscle. It contains heme-iron group associated with a single polypeptide chain. The chain containing several helical regions is further folded into a compact structure

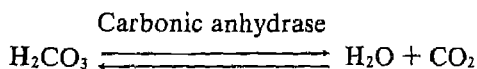
Protein denaturation may or may not be reversible. Proteins of egg-white are globular and soluble. When an egg is boiled hard, the protein is denatured and unfolds into a rubbery insoluble mass. This is irreversible denaturation and the protein cannot return to its original state. In reversible denaturation the protein unfolds in the presence of a denaturing agent like salt, but is restored to its original state upon removal of the reagent.

### 19.3.5 Enzymes

Amide links are chemically very stable. Normally, hydrolysis of amides in the laboratory requires heating the amides with alkali for a few hours. However, in a living system, proteins in food are hydrolysed quite easily to individual amino acids. How does this happen? This is because of the presence of enzymes in cells. Enzymes themselves are globular proteins that catalyse chemical reactions in living systems; they are biological catalysts. A typical cell contains about 3000 different kinds of enzymes. Unlike many reactions in a laboratory, most bio-chemical reactions in cells occur in aqueous solutions at pH around 7.0, at physiological temperatures (37°C

or 310 K) and at atmospheric pressure. Under these conditions, the reactions do not occur at appreciable rates without the catalysis by enzymes

There are two remarkable properties of enzymes, *specificity* and *efficiency*. Each enzyme catalyses only one type of chemical reaction. They speed up the reaction by factors of upto  $10^{20}$ . To get some idea of the tremendous efficiency and specificity of enzymes, let us consider the enzyme carbonic anhydrase present in the red cells of blood. This enzyme catalyses the reversible reaction, the breakdown of carbonic acid to water and carbon dioxide.



At ideal conditions, a single molecule of carbonic anhydrase is capable of catalysing the breakdown of about 36 million molecules of carbonic acid in one minute. The enzyme, carbonic hydrase, has an important role in maintaining the carbon dioxide levels in body fluids and tissues.

The success of living forms is largely due to the cell's ability to make a large number of enzymes, each specific to catalyse a particular reaction. No other type of catalyst can match the specificity and efficiency of enzymes. The deficiency of even one of the many enzymes in the body can cause a serious disease. For example, some mentally retarded children suffer from a disease known as *phenyl ketone urea*, caused by the deficiency of the enzyme PHENYLALANINE HYDROXYLASE. In some cases, this disease can be prevented by feeding the child with a properly controlled diet.

## 19.4 NUCLEIC ACIDS

One of the most amazing aspects of life is the ability of living organisms to reproduce themselves. At the most fundamental level, this reproduction is the self-duplication of a cell by division. In order that a cell live, it must have a record of amino acid sequences of all its enzymes and proteins, as they are constantly required for the production of new cells and to repair damaged cells. The differences in various species result from differences in the nature and content of their constituent proteins. Thus when a cell divides, the resulting two new cells must be provided with identical information about their proteins. How is this information stored in a cell and transmitted accurately to their offsprings? The answer to this lies in the chemical structure of another class of macromolecules called NUCLEIC ACIDS. Nucleic acids are the major constituents of the nuclei of all cells. There are two types of nucleic acids: DEOXYRIBONUCLEIC ACID (DNA) and RIBONUCLEIC ACID (RNA).

### 14.4.1 Structure of Nucleic Acids

Both DNA and RNA are polymers of NUCLEOTIDES i.e., they are POLY NUCLEOTIDES. A nucleotide consists of three chemical components, a *sugar*, a *phosphate* group and a *nitrogen base* residue (Fig. 19.5). There are four types of base residues present in DNA. Two of these bases, thymine (T) and cytosine (C) are

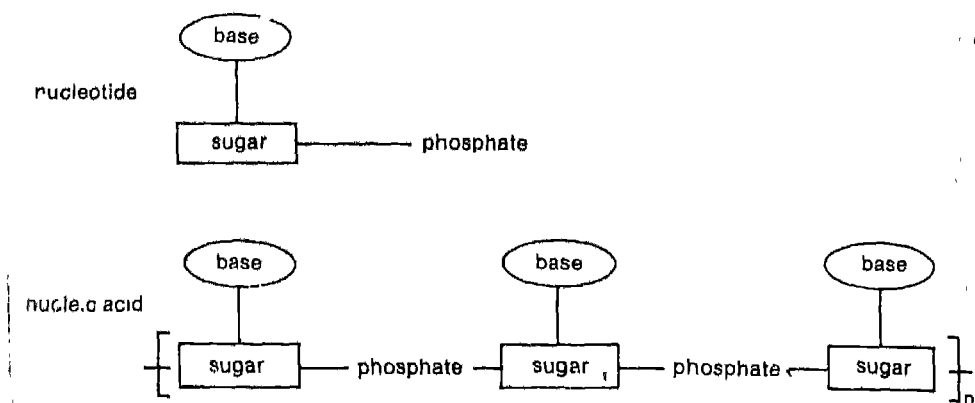


Fig. 19.5 Nucleotides are the monomeric units of nucleic acids. They consist of a nitrogen base (purine or pyrimidine) covalently linked to a sugar (ribose or deoxyribose) which in turn is attached to a phosphate.

known as PYRIMIDINE bases. The other two, adenine (A) and guanine (G), are called PURINE bases. RNA differs from DNA in two ways (a) the sugar residues in RNA is ribose whereas in DNA it is 2-deoxyribose, and (b) RNA contains the pyrimidine base URACIL (U) instead of thymine (T) in DNA.

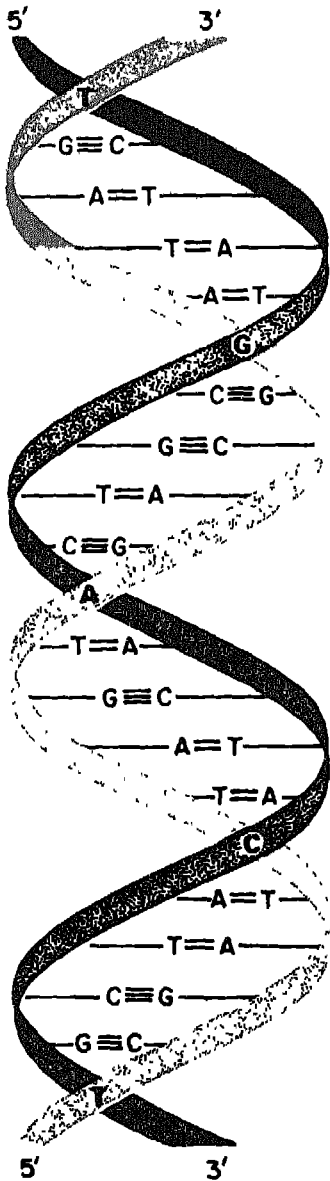
The consecutive joining of the sugar unit of one nucleotide to the phosphate group of the next nucleotide results in a long chain of nucleic acid. The nucleic acid backbone thus consists of alternating sugar-phosphate residues. Attached to each sugar residue on this backbone is one of the four base residues. The primary structure of nucleic acids refers to the sequence of base residues attached to the sugar phosphate backbone.

#### 19.4.2 The Double-Helix

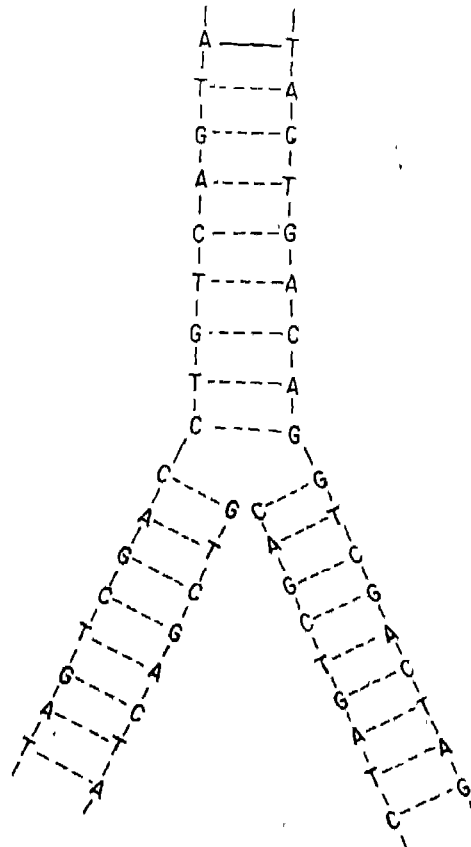
The key to understanding how DNA works lies in its three-dimensional structure. In 1953, James Watson and Francis Crick working at Cambridge, England, proposed that DNA consists of two polynucleotide chains coiled together in the form of a double-helix (Fig. 19.6). The two chains of the double-helix are held together by hydrogen bonds specifically between a purine and a pyrimidine base pair. A is linked to T with two hydrogen bonds and G is linked to C with three hydrogen bonds. The two chains are said to be *complementary* to each other, since the base sequence of one strand automatically fixes that of the other due to the above base-pairing principle. Watson and Crick's proposal of the double-helix structure of DNA is regarded as one of the most significant contributions to science in recent times.

#### 19.4.3 Biological Functions of Nucleic Acids

The two most important functions of DNA are: (i) *replication* and (ii) *protein synthesis*. Replication is the process by which a single DNA molecule produces two



**Fig. 19.6** The double helical structure of nucleic acids arises from an inter-twisted, twisted conformation of two polynucleotide strands, held together by specific hydrogen bonding between the bases.



**Fig. 19.7** The DNA during a replication process directed by complementary base pairing. For simplicity only base sequences are indicated. C and G are held together by three hydrogen bonds. A and T by two hydrogen bonds

identical copies of itself during cell division. In order to do this, the two strands of the double helix first separate and each strand serves as a template or pattern for synthesis of two new strands (Fig 19.7). Because of the base-pair specificity, the sequence of the new strand is complementary to the original. Thus replication leads to production of two identical copies of DNA from the parent DNA. A copy of each is then passed on to the two new cells resulting from cell division.

DNA also acts as an instruction manual for all *protein synthesis* in a cell. How is the information for this stored in the structure of DNA? A sequence of three bases (TRIPLET) along a DNA chain codes for a particular amino acid. Thus a particular set of triplets (Fig. 19.8) in a stretch of DNA corresponds to a particular sequence of amino acids in a protein. Each segment of the DNA molecule which codes for a complete protein is called a *gene*. The DNA found in a human cell contains about 5-50 billion nucleotide bases coding for nearly one million genes.

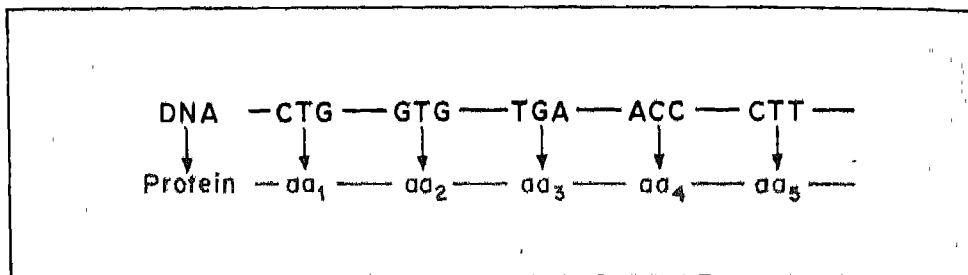


Fig 19.8 A set of triplet in a stretch of DNA molecule corresponds to a sequence of amino acids in a protein

#### 19.4.4 Viruses

Viruses are the lowest forms of life and are much smaller than bacteria. The infectious nature of viruses is responsible for many diseases of plants and animals. Viruses which infect bacteria are called bacteriophages. Influenza, mumps, measles, poliomyelitis, small pox, rabies and common cold are some of the human diseases caused by viruses.

Viruses can be considered to be living organisms as they reproduce. However, they are so simple constitutionally that they cannot multiply themselves as cells do. They first invade the host cells and take over the reproductive machinery of these cells. They then multiply within the host cells, break open and finally destroy them. The new virus particles then start the destruction of new host cells.

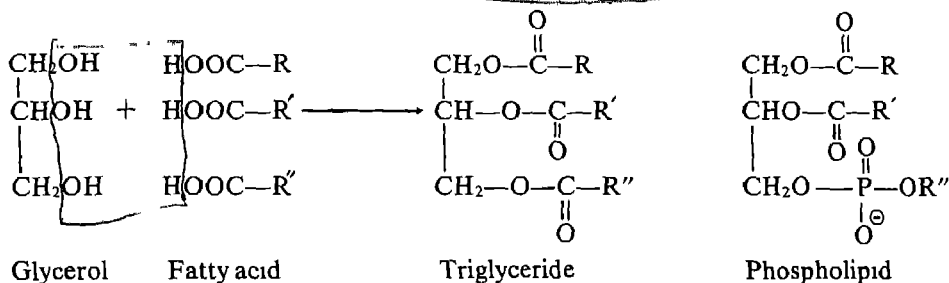
Most viruses are no more than a protein coat wrapped around a nucleic acid core. The nucleic acid can be either RNA or DNA. Some examples of RNA viruses are polio virus and tobacco mosaic virus (TMV). Bacteriophages, herpes virus and SV 40, polyoma virus (cancer-causing) are some of the DNA viruses.

#### 19.5 LIPIDS

It is possible to break cells, empty their contents and isolate only the cell *membranes*. Chemically, the cell membranes are made up of molecules, very different from carbohydrates, proteins and nucleic acids. These are the **LIPIDS**. They differ from the other class of molecules in that they are relatively water-insoluble, but soluble in organic solvents such as chloroform and ether. **WAXES, TRIGLYCERIDES and PHOSPHOLIPIDS** are the major naturally occurring lipids. **Waxes** are esters of long chain fatty acids with long chain alcohols, for example, bees wax is myricyl palmitate.

$\text{CH}_3(\text{CH}_2)_{14}-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{O}(\text{CH}_2)_{29}\text{CH}_3$  A wax coat protects surfaces of many plant leaves

from water loss and attack by micro-organisms. Waxes are used in car and floor polishes. The triesters of fatty acids with glycerol are known as TRIGLYCERIDES. These are the major components of animal fats and vegetable oils.



$\text{R}, \text{R}', \text{R}'' = \text{long chain alkyl residues}$

At room temperature, fats are solids whereas oils are liquids. Triglycerides containing unsaturated fatty acids such as oleic and linoleic acids are generally oils, those with saturated fatty acids are fats. Hydrogenation of double bonds in the presence of a catalyst converts oils into fats. This is a commercially important process in the manufacture of *Vanaspati Ghee*. Oils and fats, being esters, can be hydrolysed by alkali. This process is called saponification and results in the production of alkali salts of fatty acids. These are nothing but detergent soaps. Soap is made by heating beef tallow or coconut oil with an excess of alkali.

The lipids constituting the major components of cell membranes are PHOSPHOLIPIDS. Phospholipids are derived from glycerol in which two of the hydroxyls are linked to fatty acid molecules and the third hydroxyl is linked to a phosphate residue. The occurrence of various lipids, along with a few specific proteins give cell membranes unique structures to effectively perform their function. The function of the proteins in membranes is to facilitate the transport of ions and molecules in and out of the cell. The cell membranes are highly selective barriers which allow the nutrients to enter and the waste products to leave the cell.

### EXERCISES

- 19.1 Give a source and use of (i) starch, and (ii) cellulose
- 19.2 What is the basic structural difference between starch and cellulose?
- 19.3 What is an amide bond?

- 19.4 What is a peptide bond?
- 19.5 List three functions of proteins in the body and write a sentence about each. Give an example of each.
- 19.6 Name two important secondary structural forms for a protein. Give examples of each.
- 19.7 What is the difference between normal haemoglobin and sickle cell haemoglobin?
- 19.8 What happens when a protein is denatured?
- 19.9 Write a short note on enzymes.
- 19.10 Write the basic structure of a nucleotide.
- 19.11 (i) How does DNA differ from RNA with respect to (a) sugar, and (b) base residues?  
 (ii) Classify the following into purine or pyrimidine bases, sugars, lipids, proteins and carbohydrates:  
 thymine, adenine, triglycerides, deoxyribose, uracil, ribose, starch, guanine, sucrose, cytosine, haemoglobin, carbonic anhydrase.
- 19.12 What type of bonds hold a DNA double helix together?
- 19.13 Which of the following base pairs are found in DNA and which of them in RNA?  
 (i) A:A, (ii) A:T, (iii) C:G, (iv) G:C, (v) G:A, (vi) A:U, (vii) G:U, (viii) A:C
- 19.14 If one strand of DNA has the sequence—ATGCTTGA—what is the sequence of the complementary strand?
- 19.15 Consider a double helix. Are the base pairs:  
 (i) part of the backbone structure, (ii) inside the helix, or (iii) outside the helix.
- 19.16 What is a gene?
- 19.17 What is a triplet?
- 19.18 What are the two types of organic compounds that are produced when waxes are hydrolysed?
- 19.19 What are the saponification products of the following triglycerides?
- $$\begin{array}{c}
 \text{CH}_2 - \text{O} - \text{C} - (\text{CH}_2)_{14}\text{CH}_3 \\
 | \qquad \qquad \qquad \parallel \\
 \qquad \qquad \qquad \text{O} \\
 | \\
 \text{CH} - \text{O} - \text{C} - (\text{CH}_2)_{10}\text{CH}_3 \\
 | \qquad \qquad \qquad \parallel \\
 \qquad \qquad \qquad \text{O} \\
 | \\
 \text{CH}_2 - \text{O} - \text{C} - (\text{CH}_2)_7\text{CH} = \text{CH} - (\text{CH}_2)_7\text{CH}_3 \\
 \qquad \qquad \qquad \parallel \\
 \qquad \qquad \qquad \text{O}
 \end{array}$$
- 19.20 What happens chemically, when an oil is hydrogenated?



# APPENDIX I

## PHYSICAL CONSTANTS

<i>Constant</i>	<i>Symbol</i>	<i>Value</i>
Atomic mass unit	u	$1\,660\,56 \times 10^{-27} \text{ kg}$
Avogadro constant	$N_0$	$6\,022\,05 \times 10^{23} \text{ mol}^{-1}$
Boltzmann constant	$k = \frac{R}{N_0}$	$1.380\,66 \times 10^{-23} \text{ J K}^{-1}$
Elementary charge	e	$1.602\,19 \times 10^{-19} \text{ C}$
Faraday constant	$F = N_0 e$	$9\,648\,46 \times 10^4 \text{ C mol}^{-1}$
Gas constant	R	$8\,314\,41 \text{ J K}^{-1} \text{ mol}^{-1}$
		$0\,082\,06 \text{ L atm K}^{-1} \text{ mol}^{-1}$
Mass of an electron	$m_e$	$9\,109\,53 \times 10^{-31} \text{ kg}$
		$5\,485\,80 \times 10^{-4} u$
Mass of a neutron	$m_n$	$1.674\,95 \times 10^{-27} \text{ kg}$
		$1\,008\,66 u$
Mass of a proton	$m_p$	$1\,672\,65 \times 10^{-27} \text{ kg}$
		$1\,007\,28 u$
Planck constant	h	$6.626\,18 \times 10^{-34} \text{ J s}$
Speed of light	c	$2.997\,924 \times 10^8 \text{ m s}^{-1}$

## APPENDIX II

### ANSWERS TO SOME SELECTED PROBLEMS

1.3	(i)	0.0561
	(ii)	325.23
	(iii)	104
1.9	(b)	3.3 g
1.11	(i)	$31.3 \times 10^{24}$ atoms
	(ii)	13 atoms
	(iii)	$78 \times 10^{23}$ atoms
1.12		$8.03 \times 10^{-2}$ mol
1.14		$1.33 \times 10^{21}$ magnesium atoms
3.2	(i)	Pressure = P atm Temperature = $t^{\circ}\text{C}$ Density = $d \text{ g cm}^{-3}$ Number of moles = $n/4$
	(ii)	Pressure = P atm Temperature = $t^{\circ}\text{C}$ Density = $d \text{ g cm}^{-3}$ Number of moles = $n/2$
	(iii)	Pressure = 2 P atm Density = $2d \text{ g cm}^{-3}$ Number of moles = 2n Temperature = $t^{\circ}\text{C}$
3.3	(i)	Number of moles in flask A = $8 \times$ number of moles in flask B
	(ii)	Pressure in flask A = $4 \times$ Pressure in flask B
	(iii)	Flask B
	(iv)	Flask A
3.13		0.368 nm
4.1	(i)	$1.10 \times 10^{27}$ electrons
	(ii)	$5.48 \times 10^{-4}$ g
	(iii)	$9.63 \times 10^4$ C
4.5		589 nm
4.8	(a)	1s
	(b)	2s
	(c)	3p
	(d)	4d
	(e)	4f
8.6		$330 \text{ kJ mol}^{-1}$
8.7	(i)	$2.34 \times 10^5$ kJ
	(ii)	$3.28 \times 10^5$ kJ
	(iii)	29%
8.9	(i)	400 g
	(ii)	31 kg/year
8.10		6.5 days

- 9.6  $3 \times 10^{-7} \text{ mol L}^{-1}$
- 9.9 0.666
- 9.10  $0.068 \text{ mol}^{-1}$
- 9.11 yes
- 9.14 (i)  $Q = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$
- (ii) 3.92
- (iii) The value of  $Q$  is not equal to equilibrium constant. Therefore, equilibrium is not attained.
- 9.16 (i) 11.47
- (ii) 2.89
- 9.19  $\text{pH} = 4.5$ ,  $[\text{OH}^-] = 3.3 \times 10^{-10} \text{ mol L}^{-1}$ ; The solution is acidic
- 9.20 (i) 1.06
- (ii) 11.7
- 9.22  $4.087 \times 10^{-11}$
- 9.23 Since ionic product is larger than the  $K_{\text{sp}}$  ( $1.7 \times 10^{-6}$ ), therefore precipitation of  $\text{BaF}_2$  should occur
- 10.7 (ii)  $\text{Cr(s)} \longrightarrow \text{Cr}^{3+}(\text{aq}) + 3\text{e}^-$  (anode reaction)  
 $\text{I}_2 + 2\text{e}^- \longrightarrow$  (cathode reaction)  
 $2\text{Cr(s)} + 3\text{I}_2 \longrightarrow 2\text{Cr}^{3+} + 6\text{I}^-$  (net reaction)
- 10.8 (iii)  $\text{Cu(s)} / \text{Cu}^{2+}(\text{aq})$  and (vi)  $\text{Ag(s)} / \text{Ag}^+(\text{aq})$ , if these two half cells are combined, the total EMF would be 0.46V
- 10.9 (ii) 0.116V
- 10.10 (i)  $\text{Au}^{3+}$ ,  $\text{MnO}_4^-$  (aq),  $\text{F}_2$ (g)
- 10.12 Oxidation number of elements in  $\text{C}_6\text{H}_{12}\text{O}_6$  is as follows,  
 $\text{C} = 0$ ,  $\text{H} = +1$ ,  $\text{O} = -2$
- 18.3  $\text{C}_4\text{H}_8\text{N}_2\text{O}$
- 18.4  $\text{C}_3\text{H}_4\text{N}$
- 18.7  $\text{C}_6\text{H}_4\text{Cl}_2$
- 18.8  $\text{C}_6\text{H}_5\text{NO}_2$
- 18.10  $\text{C}_7\text{H}_6\text{O}_2$